

## PATENT ABSTRACTS OF JAP

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(54) POLYCARBONATE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polycarbonate resin composition that is excellent in electroconductivity and antistatic properties, and given good appearance molded products without any adverse effect on the intrinsic merits of polycarbonate resins such as mechanical strength, heat resistance, dimensional stability.

SOLUTION: This polycarbonate resin composition comprises 100 pts.wt. of a polycarbonate resin and 0.1-100 pts.wt. of an inorganic electroconductive substance. The polycarbonate resin is produced by a melt polycondensation process and the loss angle ( $\delta$ ) and the complex viscosity ratio ( $\eta^*$ ) in Pa.s satisfy the following relational expression (1):  $2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000$  .....(1) when they are measured at 25° C and an angular velocity of 10 rad/s.

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 CLAIMS

[Claim(s)]

[Claim 1] A polycarbonate resin constituent with which a loss angle delta which it is the resin constituent which carries out 0.1-100 weight section content of the inorganic conductivity material, and this polycarbonate resin was manufactured with scorification to the polycarbonate resin 100 weight section, and was measured on condition that temperature of 250 degrees C and angular-velocity 10 rad/s, and complex coefficient-of-viscosity  $\eta^*$  (Pa-s) are characterized by filling the following relational expression (1).

[Equation 1]

$$2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000 \dots (1)$$

[Claim 2] A polycarbonate resin constituent according to claim 1 characterized by being within the limits whose end hydroxyl-group content of polycarbonate resin is 50-1000 ppm.

[Claim 3] A polycarbonate resin constituent according to claim 1 characterized by viscosity average molecular weight of polycarbonate resin being within the limits of 12,000-30,000.

[Claim 4] A polycarbonate resin constituent given in any of claims 1-3 they are with which polycarbonate resin is characterized by being manufactured by ester interchange of bisphenol A and diphenyl carbonate.

[Claim 5] A polycarbonate resin constituent given in any of claims 1-4 characterized by inorganic conductivity material consisting of one sort chosen from a group which consists of a carbon fiber, a metal fiber, a metal powder, conductive carbon black, a carbon nanotube, and graphite, or two sorts or more of combination they are.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the polycarbonate resin constituent which was excellent in the suitable mechanical strength and the thermal resistance for housing, components, etc. of an electric electronic product, and dimensional stability, and was excellent in the appearance of conductivity, antistatic nature, and mold goods in more detail about the polycarbonate resin constituent which comes to blend inorganic conductivity material.

[0002]

[Description of the Prior Art] Polycarbonate resin is broadly used in many fields as resin excellent in a mechanical strength, thermal resistance, transparency, dimensional stability, etc. Especially, the cases used for electric electronic parts have been increasing in number very much by development of the information industry in recent years. However, since it is the insulation which originally does not conduct the electrical and electric equipment, the synthetic resin containing polycarbonate resin cannot be used for the components of which conductivity is required if it remains as it is. Moreover, there is difficulty also in using it for the electric electronic parts which dust and dust tend to adhere and dislike adhesion of dust and dust, since synthetic resin tends to be charged. As this cure, conductive material is blended with polycarbonate resin and giving conductivity and antistatic nature is performed. The polycarbonate resin which carbon fiber metallurgy group fiber and conductive carbon black were mentioned, and blended these as typical conductive material is widely used in the industrial field as which conductivity and antistatic nature including electric electronic parts are required.

[0003] However, in order to give conductivity to the polycarbonate resin which is originally insulation, it is necessary to blend most quantity of conductive material, therefore the mechanical strength, the thermal resistance, the dimensional stability, and the moldability (fluidity) of polycarbonate resin original fall, and the problem that mold-goods appearance is spoiled arises. Moreover, in recent years, the thinning of components and lightweight-ization progress, conductivity is discovered in a smaller amount, and the polycarbonate resin which suppressed the fall of a fluidity or a mechanical strength is called for. On the other hand, for example, invention concerning the constituent which blended the carbon fiber with the polycarbonate resin which has the hydroxyl group of a specific rate in a resin end is indicated by JP,2001-49109,A. However, the adhesion of polycarbonate resin and a carbon fiber was improved, the chief aim has set to raise a mechanical strength, and this invention of the conductive amelioration effect is insufficient. Moreover, it is indicated by JP,1-21185,B by blending phosphorus compounds with the constituent which consists of polycarbonate resin and a carbon fiber that conductivity improves. Although conductivity is improving by adding this component to be sure, the thermal resistance which polycarbonate resin originally has is spoiled, or we are anxious about generating of the mold deposit by combination of a low-molecular object etc.

[0004] Furthermore, although it will be difficult to give conductivity about the case where it is blended with polycarbonate resin, the conductive material, for example, the conductive carbon black, other than a carbon fiber, with a mechanical strength and thermal resistance held and the aggregate accompanying the maldistribution of carbon black will occur, it is in the condition which what knowledge does not have, either about such amelioration technique. The polycarbonate resin constituent excellent in the appearance of conductivity, antistatic nature, and mold goods was called for under this condition, without spoiling the mechanical strength of polycarbonate resin original, thermal resistance, and dimensional stability in any way.

[0005].

[Problem(s) to be Solved by the Invention] This invention offers the polycarbonate resin constituent excellent in the appearance of conductivity, antistatic nature, and mold goods, without spoiling the mechanical strength of polycarbonate resin original, thermal resistance, and dimensional stability in any way.

[0006]

[Means for Solving the Problem] As a result of repeating examination wholeheartedly that said technical problem should be solved, this invention persons to a surprising thing A resin constituent which blended inorganic conductivity material with polycarbonate resin which is obtained by specific process and has specific melting viscoelasticity Distribution of inorganic conductivity material came to complete a header and this invention for it being very good and excelling in appearance of conductivity and mold goods, without sacrificing a mechanical strength and thermal resistance compared with polycarbonate resin which has the property of an and also [ molecular weight is an EQC substantially ]. That is, a summary of this invention is a resin constituent which carries out 0.1-100 weight section content of the inorganic conductivity material to the polycarbonate resin 100 weight section, and the loss angle delta which this polycarbonate resin was manufactured with scorification, and was measured on conditions with a temperature [ of 250 degrees C ] and an angular velocity of ten rads [ /s ], and complex coefficient-of-viscosity  $\eta^*$  (Pa-s) consist in a polycarbonate resin constituent characterized by filling the following relational expression (1).

[0007]

[Equation 2]

$$2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000 \dots (1)$$

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained concretely. It is required for the loss angle delta measured on conditions with a temperature [ of 250 degrees C ] and an angular velocity of ten rads [ /s ] and complex coefficient-of-viscosity  $\eta^*$  (Pa-s) to fill the following relational expression (1), it is the range of the following relational expression (2) preferably, and the polycarbonate resin used for this invention constituent is the range of the following relational expression (3) still more preferably. this invention -- setting -- this -- the value of  $\tan \delta / \eta^* - 0.87$  was used as a parameter which shows the melting viscoelasticity of polycarbonate resin. When the value of  $\tan \delta / \eta^* - 0.87$  exceeds the case of less than 2500, or 6000, the maldistribution of inorganic conductivity material occurs, and the appearance of a fluidity, conductivity, and mold goods is spoiled.

[0009]

[Equation 3]

$$2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000 \dots (1)$$

$$2800 \leq \tan \delta / \eta^* - 0.87 \leq 5500 \dots (2)$$

$$3000 \leq \tan \delta / \eta^* - 0.87 \leq 5000 \dots (3)$$

[0010] Generally the loss angle delta is known as one of the indexes which expresses the delay of the phase of the strain over stress searched for from measurement of dynamic melting viscoelasticity, and expresses a dynamic viscoelasticity action.  $\delta$  ( $\tan \delta$ ) shows that the viscosity-property of viscoelasticity is strong when the value is large, and when small, it shows that an elastic property is strong. The factor which determines this value is complicated, for example, the molecular structure including branching structures, such as a class of polycarbonate resin manufacture raw material (monomer including copolymerization), a copolymerization presentation, structure of a copolymer, and the number of the branch points, the length of branched chain, etc., molecular weight, molecular weight distribution, etc. are mentioned.

[0011] According to examination of this invention persons, the polycarbonate resin manufactured by the interface method using the conventional phosgene had the problem that get worse extremely, and inorganic conductivity material came up to the mold-goods surface, or a fluidity condensed further at the time of injection molding, and spoiled the appearance of mold goods, when inorganic conductivity material was added. if the polycarbonate resin manufactured by such interface method plots the value of  $\delta$  ( $\tan \delta$ ) to the logarithmic coordinates to the complex coefficient of viscosity ( $\eta^*$  (Pa-s)) which is indexes, such as molecular weight, --  $\tan \delta / \eta^* - 0.87$  -- it turned out that it stands in a line mostly on the straight line of about 8000. (Here,  $-0.87$  which is the characteristic of  $\eta^*$  expresses the above-mentioned slope of a line, and  $\tan \delta / \eta^* - 0.87$  express the value of  $\tan \delta$  when extrapolating the

above-mentioned straight line to  $\eta = 1$  (Pa-s). That is, it becomes possible to eliminate the molecular weight (viscosity) dependency of a loss angle by using the value of  $\tan \delta / \eta = 0.87$  for a parameter. .  
 [0012] On the other hand, the polycarbonate resin which has that the polycarbonate resin manufactured by scorification generally does not ride on this straight line and scorification polycarbonate resin in the range of  $2500 \leq \tan \delta / \eta = 0.87 \leq 6000$  although mold-goods appearance is [ that a flow pattern tends to come out of the thing of  $\tan \delta / \eta = 0.87 < 2500$  at the time of injection molding ] inferior found out that the appearance of a fluidity and mold goods was excellent also in the range where molecular weight is large.

[0013] the stress with which the one where the value of  $\delta$  ( $\tan \delta$ ) is smaller pushes polycarbonate resin against the mold-goods surface by it by the normal stress of polycarbonate resin becoming large as an effect which the polycarbonate resin specified with this melting viscoelasticity parameter gives to a fluidity in this invention -- high -- consequently, condensation and the mold-goods surface of inorganic conductivity material -- it looms and it is presumed that  $\delta$  decreases remarkably. Moreover, in addition to this, the fluidity for a thin-walled part becomes high, and it is effective in a moldability being improved. However, when the value of  $\delta$  ( $\tan \delta$ ) is too small, if certain, although there is nothing, a flow pattern occurs on the mold-goods surface, and a reason is not desirable.

[0014] In addition, in this invention, although what could also add various stabilizers, the ultraviolet ray absorbent, the release agent, the coloring agent, etc. to polycarbonate resin, may add these additives before pellet manufacture in the middle of manufacture of polycarbonate resin, and generally contained those additives may be called "polycarbonate resin", the value of the above-mentioned relational expression specified by this invention is calculated about the polycarbonate resin which does not contain these additives at all.

[0015] It is desirable that it is 50-1000 ppm, as for the end OH radical content of the polycarbonate resin used for this invention, it is still more desirable that it is 70-800 ppm, and it divides and is desirable that it is 90-600 ppm. When an end OH radical content exceeds 1000 ppm, thermal stability and hydrolysis-proof nature get worse, and when too few, there is orientation for manufacture of the polycarbonate resin of desired molecular weight to become difficult.

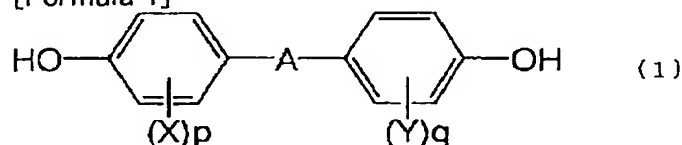
[0016] When the molecular weight of polycarbonate resin is low, although excelled in a fluidity, it is inferior to a mechanical strength. On the contrary, when the molecular weight of polycarbonate resin is high, although excelled in a mechanical strength, it is inferior to a fluidity. In this invention, the polycarbonate resin of 12,000-30,000 has desirable viscosity average molecular weight, the polycarbonate resin of 14,000-26,000 has still more desirable viscosity average molecular weight, and the polycarbonate resin of 16,000-24,000 has the most desirable viscosity average molecular weight.

[0017] The polycarbonate resin concerning this invention is manufactured by scorification, and if it is resin which has the rate of viscoelasticity which fills the above-mentioned formula (1), although especially the process is not limited, an aromatic series dihydroxy compound and carbonic acid diester can be manufactured as a raw material, for example as following.

[0018] Aromatic series dihydroxy compound: The aromatic series dihydroxy compound which is one of the raw materials of the polycarbonate resin of this invention is shown by the following formula (1).

[0019]

[Formula 1]



[0020] (A is a divalent radical shown by the shape of single bond and a straight chain of the carbon numbers 1-10 which may be replaced, the letter of branching, an annular divalent hydrocarbon group or -O-, -S-, -CO-, or -SO<sub>2</sub>- among a formula (1), X and Y are the hydrocarbon groups of a halogen atom or carbon numbers 1-6, and q is the integer of p and 0, or 1.) In addition, X, Y, and p and q may be the same, or may differ from each other mutually, respectively. .

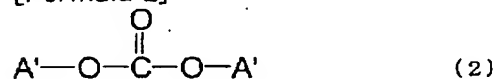
[0021] As a typical aromatic series dihydroxy compound For example, screw (4-hydroxyphenyl) methane, 2, and 2-screw (4-hydroxyphenyl) propane, 2 and 2-screw (4-hydroxy-3-methylphenyl) propane, 2, and 2-screw (4-hydroxy-3-t-butylphenyl) propane, 2 and 2-screw (4-hydroxy - 3, 5-dimethylphenyl) propane, 2 and 2-screw (4-hydroxy - 3, 5-dibromo phenyl) propane, 4 and 4-screw (4-hydroxyphenyl) heptane, 1, and

1-screw (4-hydroxyphenyl)lohexane, 4, a 4'-dihydroxy biphenyl, 3, 5, 5'-tetramethyl - 4 4'-dihydroxy biphenyl, A screw (4-hydroxyphenyl) sulfone, a screw (4-hydroxyphenyl) sulfide, the screw (4-hydroxyphenyl) ether, a screw (4-hydroxyphenyl) ketone, etc. are mentioned. These aromatic series dihydroxy compounds are independent, or two or more sorts can be mixed and used for them. Also in these, 2 and 2-screw (4-hydroxyphenyl) propane (hereafter, it may also be called "bisphenol A" and may be written as "BPA") is desirable.

[0022] Carbonic acid diester: The carbonic acid diester which is other one of the raw materials is shown by the following formula (2).

[0023]

[Formula 2]



[0024] (A' is the shape of a straight chain, the letter of branching, or the annular univalent hydrocarbon group of the carbon numbers 1-10 which may be replaced among a formula (2), and two A' may be the same or may differ mutually.) The dialkyl carbonate represented by the substitute diphenyl carbonate represented by diphenyl carbonate, JITORIRU carbonate, etc., dimethyl carbonate, diethyl carbonate, G t-butyl carbonate, etc. as typical carbonic acid diester, for example is mentioned. These carbonic acid diester is independent, or two or more sorts can be mixed and used for it. Also in these, diphenyl carbonate (it may be hereafter written as "DPC") and substitute diphenyl carbonate are desirable.

[0025] Moreover, the above-mentioned carbonic acid diester may replace the amount not more than 30 mol % with dicarboxylic acid or dicarboxylic acid ester preferably [ it is desirable and ] to the 50 mol % less or equal and a pan. As typical dicarboxylic acid or dicarboxylic acid ester, a terephthalic acid, isophthalic acid, terephthalic-acid diphenyl, isophthalic acid diphenyl, etc. are mentioned. Polyester carbonate is obtained when it replaces with such dicarboxylic acid or dicarboxylic acid ester. These carbonic acid diester (the ester of the dicarboxylic acid which the above replaced, or dicarboxylic acid is included.) It is below the same. It is usually superfluously used to an aromatic series dihydroxy compound, namely, an aromatic series dihydroxy compound -- receiving -- a mole ratio -- 1.001-1.3 -- it is preferably used within the limits of 1.01-1.2. Although the end OH radical of polycarbonate resin will decrease if the end OH radical of the polycarbonate resin manufactured when the mole ratio became smaller than 1.001 increases, and thermal stability and hydrolysis-proof nature get worse and a mole ratio becomes large from 1.3, the speed of an ester exchange reaction falls and there is orientation for manufacture of the polycarbonate resin of desired molecular weight to become difficult under the same conditions. In this invention, it is good to use the polycarbonate resin adjusted to the range whose end OH radical content is 50-1000 ppm.

[0026] As the supply method of the raw material to a raw material mixing chamber, in order that the direction of a liquid condition may tend to maintain measuring precision highly, it is desirable to carry out melting of one side or both, and to supply them in the state of a liquid among an aromatic series dihydroxy compound and carbonic acid diester. When supplying a raw material in the state of a liquid, as a metering installation, an oval flow meter, a micro motion type flowmeter, etc. can be used. When supplying a raw material by the solid state, it is desirable to use what measures weight, and although weight feeders, such as a \*\* RUTO type and a loss in wait type, can be used, especially a loss in wait method is on the other hand, more desirable than what measures capacity like a screw-type feeder.

[0027] Ester interchange catalyst: In case polycarbonate resin is manufactured with scorification, a catalyst is usually used. In the method of manufacturing the polycarbonate resin concerning this invention, although there is no limit in a catalyst kind, generally basic compounds, such as an alkali metal compound, an alkaline-earth-metal compound, a basic boron compound, basic phosphorus compounds, a basic ammonium compound, or an amine system compound, are used. These may be used by one kind and may be used combining two or more kinds.

[0028] the amount of the catalyst used -- one mol of aromatic series dihydroxy compounds -- receiving -- 0.05-5micro mol -- desirable -- 0.08-4micro mol -- it is used within the limits of 0.1-2micro mol still more preferably. Polymerization activity required to manufacture the polycarbonate resin of desired molecular weight if there is less amount of the catalyst used than the amount of above is not acquired, but when [ than this amount ] more, a polymer hue gets worse, and branching-ization of polymer also progresses, and there is orientation for the fluidity at the time of shaping to fall.

[0029] As an alkali metal compound, there are organoalkali metal compounds, such as inorganic alkali metal compounds, such as a lithium, sodium, a potassium, a rubidium, a hydroxide of caesium, a carbonate, and carbonic acid hydride, an alcoholate, a phenolate, and organic carboxylate, etc. Also in these alkali metal compounds, a caesium compound is desirable, and if the concrete most desirable caesium compound is mentioned, they will be cesium carbonate, carbonic acid hydrogen caesium, and cesium hydroxide.

[0030] Moreover, as an alkaline earth metal compound, there are organoalkaline earth metal compounds, such as inorganic alkaline earth metal compounds, such as beryllium, magnesium, calcium, strontium, a hydroxide of barium, and a carbonate, an alcoholate, a phenolate, and organic carboxylate, etc.

[0031] As a basic boron compound, for example Tetramethyl boron, tetraethyl boron, Tetra-propyl boron, tetrabutyl boron, trimethyl ethyl boron, Trimethyl benzyl boron, trimethyl phenyl boron, triethyl methyl boron, Triethyl benzyl boron, triethyl phenyl boron, tributyl benzyl boron, Tributyl phenyl boron, tetra-phenyl boron, benzyl triphenyl boron, Sodium salt, such as methyl triphenyl boron and butyl triphenyl boron, potassium salt, lithium salt, a calcium salt, magnesium salt, barium salt, or a strontium salt is mentioned.

[0032] As basic phosphorus compounds, the 4th class phosphonium salt guided from trivalent phosphorus compounds, such as a triethyl phosphine, a tri-n-propyl phosphine, a tri-i-propyl phosphine, tri-n-butyl phosphine, triphenyl phosphine, and tributyl phosphine, or these compounds is mentioned, for example.

[0033] As a basic ammonium compound, for example Tetramethylammonium hydroxide, Tetraethylammonium hydroxide, tetrapropylammonium hydroxide, Tetrabutylammonium hydroxide, trimethyl ethylammonium hydroxide, Trimethyl benzyl ammonium hydroxide, trimethyl phenyl ammonium hydroxide, Triethyl methylammonium hydroxide, triethyl benzyl ammonium hydroxide, Triethyl phenyl ammonium hydroxide, tributyl benzyl ammonium hydroxide, Tributyl phenyl ammonium hydroxide, tetra-phenyl ammonium hydroxide, Benzyl triphenyl ammonium hydroxide, methyl triphenyl ammonium hydroxide, butyl triphenyl ammonium hydroxide, etc. are mentioned.

[0034] As an amine system compound, 4-aminopyridine, 2-aminopyridine, N, and N-dimethyl-4-aminopyridine, 4-diethylamino pyridine, 2-hydroxypyridine, 2-methoxy pyridine, 4-methoxy pyridine, 2-dimethylamino imidazole, 2-methoxy imidazole, an imidazole, 2-mercaptoimidazole, 2-methylimidazole, an amino quinoline, etc. are mentioned, for example. An alkali metal compound is desirable practical among these catalysts.

[0035] The above-mentioned ester interchange catalyst is used with the gestalt of the catalyst solution which dissolved in the solvent. As a solvent, the solvent which dissolves a raw material aromatic series dihydroxy compound besides water, an acetone, alcohol, toluene, and a phenol and coal-for-coke-making acid diester is mentioned, for example. In these, water is desirable, and when making especially an alkali metal compound into a catalyst, considering as an aqueous solution is suitable.

[0036] The manufacture method of polycarbonate resin: Although it will not be especially limited if the method of manufacturing polycarbonate resin from an aromatic series dihydroxy compound and carbonic acid diester is scorification and it is the method by which the polycarbonate resin which has said specific physical properties is obtained, the following methods are adopted, for example. That is, by a raw material mixing chamber etc., after agitating both raw materials to homogeneity, a catalyst is added, a polymerization is performed and polycarbonate resin is usually produced. For example, it is desirable to supply continuously the above-mentioned aromatic series dihydroxy compound and both the raw materials of carbonic acid diester to a raw material mixing chamber, and to supply the obtained mixture and an ester interchange catalyst to a polymerization tank continuously. In order to be stabilized and to produce the polycarbonate resin of the above-mentioned specific physical properties of this invention in that case, the method of satisfying the following (a) and both the conditions of (b) at least is adopted, for example.

[0037] (a) Choose from within the limits of 0.05 – 5micro mol the "amount of setting catalysts" which is the aim catalyst amount of supply for keeping constant the amount of catalysts to the aromatic series dihydroxy compound or one mol of carbonic acid diester supplied to a polymerization tank for every unit production time which carried out fractionation of all the production time to one or more to one mol of aromatic series dihydroxy compounds. In addition, with "all production time", it corresponds to the feeding time amount which produces polycarbonate resin stably in a polymerization tank, and the polycarbonate resin production time at the time of the astables at the time of manufacture termination etc. does not contain at the time of starting and a grade change.

(b) The actual amount of ester interchange catalysts (only henceforth "the actual amount of catalysts") to which at least 95% of time amount of each unit production time is supplied is maintained to one mol of aromatic series dihydroxy compounds by the value within each the amount mol of  $\geq 0.1$ micro of setting



catalysts. In the above (a), though all production time, it is not necessary to be necessarily constant value, fractionation of all the production time is carried out to one or more, and the amount of setting catalysts can be set up for every unit production time of the.

[0038] Hereafter, when this method is explained in detail and all production time is the unit production time of single fractionation, as for at least 95% of that time amount, the actual amount of catalysts is maintained to one mol of aromatic series dihydroxy compounds to the value within the amount mol of  $\leq 0.1$  micro of setting catalysts. Moreover, when fractionation of all the production time is carried out to two or more unit production time and the amount of setting catalysts is changed, at least 95% of time amount of each unit production time maintains the actual amount of catalysts to the value within each the amount mol of  $\leq 0.1$  micro of setting catalysts. In any case, it is desirable to maintain within the amount mol of  $\leq 0.08$  micro of setting catalysts, and it is desirable. [ of especially the thing to maintain within the amount mol of  $\leq 0.06$  micro of setting catalysts ] Furthermore, the rate of time amount that the actual amount of catalysts is maintained by the controlled value is more desirable so that it is close to 100%, although what is necessary is just all production time or at least 95% of each unit production time. If it becomes time amount fewer than 95%, the polycarbonate resin of desired molecular weight and an end OH radical content will no longer be obtained. When there are many rates of time amount especially with more amounts of catalysts than the amount of setup, the polycarbonate resin hue acquired gets worse, and it carries out that branching-ization of polycarbonate resin progresses etc., and there is orientation for the fluidity when what satisfies the relational expression specified by this invention as a result no longer being obtained, and fabricating this polycarbonate resin to also fall. In addition, although it is possible to manufacture the polycarbonate resin of this invention even if it changes the manufacture conditions of polymerization reaction time, such as whenever [ polymerization temperature polymerization time amount, and reduced pressure ], it is thought that stable production becomes difficult. It turned out that the actual amount of catalysts is maintained within the amount mol of  $\leq 0.1$  micro of setting catalysts, and a very small fluctuation range, the specific relational expression specified by this invention is satisfied, without needing complicated polymerization actuation for the first time by continuing supply, and polycarbonate resin excellent in many physical properties, such as narrow molecular weight distribution, a color tone, a fluidity, thermal resistance, and machine physical properties, can be stably produced now.

[0039] It is desirable to use an oval flow meter, a micro motion type flowmeter, etc., and to measure and supply the catalyst flow rate which supplies it to a polymerization tank in order to make the value within the amount mol of  $\leq 0.1$  micro of setting catalysts maintain the aforementioned actual amount of catalysts. In order to control catalyst supply automatically, the setting catalyst flow rate first computed from the amount of supply to the raw material preparation tub of the amount of setting catalysts, the aromatic series dihydroxy compound, or carbonic acid diester which inputted and mentioned above the measured value of a continuously actual catalyst flow rate to the computer is measured. When the measured value of an actual catalyst flow rate differs from this setting catalyst flow rate in that case, this result is told to catalyst measuring and a feeder, and the opening of a bulb etc. is adjusted, and it controls so that an actual catalyst flow rate and a setting catalyst flow rate are in agreement.

[0040] If rationalization of the time between measurements of an actual catalyst flow rate is considered enough, it is possible to control like [ the control based on continuous intermittent measurement ] continuous measurement, but in order to obtain the product of the stable quality, as for the automatic control of catalyst supply here, it is desirable that it is continuous automatical measurement. That is, if a catalyst flow rate can be measured automatically continuously, since become possible to control quickly and continuously the catalyst amount of supply to a polymerization tank, consequently it is maintained by the fixed setting catalyst flow rate, and deflection, such as viscosity average molecular weight of polycarbonate resin and an end OH radical content, is small, and molecular weight distribution become narrow and a product with many still more uniform physical properties, such as a color tone, a fluidity, thermal resistance, and machine physical properties, is obtained, it is desirable. In the unit production time of a certain amount of setting catalysts, it can be easily judged [ how much / the actual amount of catalysts ] from the measurement result by the above-mentioned measurement means to the value within the amount mol of  $\leq 0.1$  micro of setting catalysts whether time amount existence was recognized. In continuous measurement, it is judged by finding the accumulation time amount which is within the amount mol of  $\leq 0.1$  micro of catalysts beforehand set up from the curve which shows the relation between an actual raw material mole ratio and the measuring time, and the accumulation time amount which shifted rather than  $\leq 0.1$  micro mol whether at least 95% of time amount of the unit production time in this amount



of setting catalysts was maintained by the value within  $\pm 0.1$  micro mol. It is continuous measurement even when it is not continuous measurement, it can judge by the method of carrying out statistics processing of this etc.

[0041] The reaction of two or more steps (ester exchange reaction) of polymerization reactions of polycarbonate resin in two or more polymerization tanks, i.e., usually carry out continuously at 3-7 steps of multistage production processes, is desirable. As a concrete reaction condition, it considers as the range for temperature: 150-320 degree C, pressure: ordinary pressure -2Pa, and mean-flow-time: 5 - 150 minutes, and in order to make more effective discharge of a phenol which carries out a byproduction with advance of a reaction in each polymerization tank, it is gradually set more as an elevated temperature and a twist high vacuum within the above-mentioned reaction condition. In order to prevent debasement, such as a hue of the polycarbonate resin obtained, a setup of low temperature and the shortest possible residence time is desirable as much as possible. In addition, as for the automatic control of the actual amount of catalysts in the case of using two or more polymerization tanks at a multistage production process, it is desirable to control the amount of supply of a catalyst automatically continuously, and it needs to have completed measurement and control less than to 1/3 of the residence time of the 1st polymerization tank in that case.

[0042] the equipment used in the above-mentioned ester exchange reaction -- a vertical type, a juxtaductal type, or a column -- you may be which format of type and a horizontal type. Usually, a turbine blade, a paddle aerofoil, a support aerofoil, a full zone aerofoil (Shinko Pantec Co., Ltd. make), The Sun Moeller aerofoil (Mitsubishi Heavy Industries, Ltd. make), the Max blend aerofoil (Sumitomo Heavy Industries, Ltd. make), One or more vertical-type polymerization tanks possessing a helical ribbon aerofoil, a torsion grid aerofoil (Hitachi Make), etc. are followed. A polymerization tank horizontal-type 1 shaft type [ , such as a disk mold and a cage mold, ], HVR and SCR, N-SCR (Mitsubishi Heavy Industries, Ltd. make), A BAIBO rack (Sumitomo Heavy Industries, Ltd. make), a glasses aerofoil, a grid aerofoil (Hitachi Make), Or the horizontal-type 2 shaft type polymerization tank possessing what combined the aerofoil which gave the feed function of a glasses aerofoil and polymer, for example, the aerofoil and/or inclination containing torsion, a twist, etc. attach can be used.

[0043] In the polycarbonate resin manufactured by the above-mentioned method, low molecular weight compounds which carry out a byproduction by the raw material monomer, the catalyst, and the ester exchange reaction, such as an aromatic series hydroxy compound and polycarbonate resin oligomer, usually remain. Especially, there are many amounts of residuals, and since a raw material monomer and an aromatic series hydroxy compound have a bad influence on physical properties, such as heat-resistant aging nature and hydrolysis-proof nature, it is desirable [ a hydroxy compound ] to be removed on the occasion of commercial production. There is no method of removing them, for example, it may devolatilize especially a limit continuously with a vent-type extruder. In that case, by adding an acid compound or its precursor and carrying out deactivation of the basic ester curing catalyst which remains in resin beforehand, the side reaction under devolatilization can be suppressed and a raw material monomer and an aromatic series hydroxy compound can be removed efficiently.

[0044] There is especially no limit in the acid compound to add or its precursor, and all can be used if there is an effect which neutralizes the basic ester curing catalyst used for a polycondensation reaction. Specifically A hydrochloric acid, a nitric acid, a boric acid, a sulfuric acid, a sulfurous acid, a phosphoric acid, phosphorous acid, Hypophosphorous acid, polyphosphoric acid, an adipic acid, an ascorbic acid, an aspartic acid, An azelaic acid, adenosine phosphate, a benzoic acid, a formic acid, a valeric acid, a citric acid, A glycolic acid, glutamic acid, a glutaric acid, a cinnamic acid, a succinic acid, an acetic acid, A tartaric acid, oxalic acid, p-toluene sulfinic acid, p-toluenesulfonic acid, Broensted acid and its ester, such as a naphthalene sulfonic acid, a nicotinic acid, a picric acid, picolinic acid, a phthalic acid, a terephthalic acid, a propionic acid, benzenesulfinic acid, benzenesulfonic acid, a malonic acid, and a maleic acid, are mentioned. These may be used independently or may be used combining two or more sorts. P-toluenesulfonic-acid methyl, a sulfonic-acid compound, or the ester compound, for example, p-toluenesulfonic acid, especially p-toluenesulfonic-acid butyl, etc. are desirable among these acid compounds or the precursor of those.

[0045] the amount of neutralization of the basic ester curing catalyst which used the addition of these acid compounds or the precursor of those for the polycondensation reaction -- receiving -- a 0.1 to 50 time mol -- it adds in the range of a mol 0.5 to 30 times preferably. As a stage to add an acid compound or its precursor, as long as it is after a polycondensation reaction, it may be good at any time and which methods, such as a method which there is nothing and is directly added according to the description of an

acid compound or its precursor or desired conditions, the method of mixing in a suitable solvent and adding, and the method of using the masterbatch of the shape of a pellet or a flake, may be used for a limit special also to the addition method. A monopodium or two shafts are sufficient as the extruder used for devolatilization. Moreover, as a twin screw extruder, it may be an engagement mold twin screw extruder, and this direction rotation or the different direction rotation is sufficient as a hand of cut. For the purpose of devolatilization, what has the vent section after the acid compound addition section is desirable. Although there is no limit in the number of vents, two to ten steps of multistage vents are usually used. Moreover, in this extruder, if needed, additives, such as a stabilizer, an ultraviolet ray absorbent, a release agent, and a coloring agent, can be added, and it can also knead with resin.

[0046] As inorganic conductivity material blended with the polycarbonate resin constituent of this invention, the well-known inorganic conductivity material blended with thermoplastics can usually be used. If an example is given, the compound conductivity material which carried out the coat of the metal will be mentioned to the surface of the inorganic conductivity material of metal systems, such as conductive material of carbon systems, such as carbon black, a carbon fiber, graphite, a carbon whisker, and a carbon nanotube, a metal fiber, metal powder, and a metallic oxide, a carbon fiber, or a whisker and a glass fiber. Also in these, a carbon fiber, a metal fiber, metal powder, conductive carbon black, a carbon nanotube, and graphite are desirable, and these can use together independent or two sorts or more.

[0047] What was generally manufactured by baking as a carbon fiber used by this invention by using an acrylic fiber, petroleum or a carbon system special pitch, cellulose fiber, a lignin, etc. as a raw material is mentioned, and a base material is not asked especially although there is a thing of various types, such as quality of fire resistance, carbonaceous, or graphite. Furthermore, in order to improve the conductivity of a carbon fiber, the carbon fiber which carried out the metal coat on the surface of the carbon fiber may be used. The metals used for the surface coat of a carbon fiber are one or more sorts of metals, such as copper, nickel, silver, cobalt, aluminum, and iron, and the method of a metal coat has well-known vacuum deposition, well-known plating, etc. The average of the aspect ratio (fiber length/diameter of fiber) of a carbon fiber is ten or more preferably. Conductivity, and reinforcement and rigidity fall that the average of an aspect ratio is less than ten. The average of the aspect ratio (fiber length/diameter of fiber) of a carbon fiber is 50 or more preferably. since the path of a carbon fiber is 3-15 micrometers, in order to adjust it to such an aspect ratio generally -- anything of configurations, such as a chopped strand, a roving strand, and a milled fiber, -- it can be used -- one sort -- or two or more sorts can be mixed and it can also use. Since the surface of a carbon fiber increases compatibility with resin unless the property of the constituent of this invention is spoiled, surface treatment, for example, silanizing, epoxy processing, urethane processing, oxidation treatment, etc. may be performed. As such a carbon fiber, it is marketed from Mitsubishi Chemical, Inc., for example by the trade name of BESUFAITO in a diamond lead and Toho Rayon Co., Ltd.

[0048] the graphite used for this invention constituent -- a natural scale-like graphite, a natural earthy graphite, an artificial graphite, etc. -- it is -- them -- one sort -- or two or more sorts can use it, mixing. As for the mean particle diameter of a graphite, what a 5-100-micrometer thing is desirable, and is 5-80 micrometers in a weighted mean is still more desirable, and its 5-60-micrometer thing is the most desirable. The eat lump by the screw worsens and a graphite with a mean particle diameter of less than 5 micrometers does not have it in measuring instability, when carrying out melting kneading using an extruder etc. [ desirable ] If mean particle diameter exceeds 100 micrometers, the appearance and dispersibility of mold goods are inferior and it is not desirable. As commercial graphite, carbon flake #585 of Nippon Sheet Glass Co., Ltd., CP of Japanese Graphite, CPB, CPB3 of China-Vietnam Graphite, CPB-30, and CPB-3000 grade are mentioned.

[0049] The conductive carbon black used for this invention constituent has desirable DBP (dibutyl phthalate) oil absorption of 100ml of 2414 to ASTM-D88 convention / thing 100g or more. If DBP oil absorption uses carbon black (100ml / less than 100g), the rate of addition of the carbon black for giving antistatic nature causes [ become high and ] the fall of a fluidity or a mechanical strength and is not desirable. as commercial conductive carbon black -- the diamond black (furnace black) of Mitsubishi Chemical, Inc., and DIN of Electrochemistry -- a turnip -- there is the Balkan Peninsula C of a rack (acetylene black), KETCHIEN black 600JD of LION, Inc., and Cabot Corp. etc.

[0050] What was manufactured from copper, brass, zinc, stainless steel, aluminum, nickel, magnesium, iron, gold, and silver can be used for the metal fiber used by this invention by the coil strip cutting method, the wire drawing drawing method, the melt spinning method, and the wire cutting method. 3-100 micrometers of

diameters of a metal fiber 5–50 micrometers preferably, and number mean fiber length is 0.3–3mm preferably 0.1–5mm.

[0051] The metal powder used by this invention can use what was manufactured from copper, brass, zinc, stainless steel, ALUMINIUM, nickel, magnesium, iron, gold, and silver. The mean particle diameter of a metal powder has desirable 0.5–20 micrometers, and since impact strength will fall and a fluidity will fall in less than 0.5 micrometers if 20 micrometers is exceeded, it is not desirable. Surface treatment may be carried out also to the metal fiber and metal powder which are used by this invention by for example, the silane system coupling agent or the titanate system coupling agent, and you may use.

[0052] It is carbon fibril which has hollow structure, as for the carbon nanotube used by this invention, it is desirable that they are the outer diameter of 3.5–70nm and five or more aspect ratios, and especially its thing that are the outer diameter of 4–60nm and ten or more aspect ratios is desirable. The conductivity of the resin constituent which will be obtained if a fibril outer diameter is inferior to the dispersibility to the inside of resin in a less than 3.5nm object and exceeds 70nm is dissatisfied. Moreover, the conductivity of the resin constituent with which an aspect ratio is obtained less than by five is dissatisfied.

[0053] A carbon nanotube is cylinder-like fibril at the essential target with which it has the outside field which essentially consists of a continuous a large number layer and internal hollow field of the carbon atom arranged regularly, and each class and a hollow field are substantially arranged around the cylinder shaft of this fibril at this heart. Furthermore, the carbon atom arranged regularly [ the above-mentioned outside field ] is a graphite-like, and it is desirable that the diameter of the above-mentioned hollow field is 2–20nm. This carbon nanotube is indicated in detail by \*\*\*\*\* No. 500943 [ 62 to ], and the U.S. Pat. No. 4,663,230 specification. About the process, a transition-metals content particle (for example, the iron which uses an alumina as a base material, cobalt, a nickel content particle) is contacted at carbon content gas, such as CO and a hydrocarbon, and a 850–1200-degree C elevated temperature, and the method of making it grow up fibrous as an origin is mentioned [ transition metals ] in the carbon produced by the pyrolysis as indicated by the above-mentioned patent official report and the United States Patent specification. This carbon nanotube is marketed by the trade name of "graphite fibril", and is easily more nearly available than high pressure KATARISHISU.

[0054] Although the loadings of the inorganic conductivity material in this invention constituent change with classes of conductive material, they are usually chosen from the range of the 0.1 – 100 weight section to the polycarbonate resin 100 weight section. In the case of carbon fiber metallurgy group fiber, concrete loadings have desirable 5 – 50 weight section, and, in the case of conductive carbon black or a carbon nanotube, its 0.5 – 20 weight section is desirable. If the loadings of inorganic conductivity material are under the 0.1 weight section, conductivity is not enough, and if the 100 weight sections are exceeded, difficulty generates and is not desirable to a moldability.

[0055] this invention constituent can also blend additives, such as other thermoplastics, a flame retarder, a shock-proof amelioration agent, an antistatic agent, a slipping agent, an anti blocking agent, lubricant, an antifogger, natural oil, synthetic oil, a wax, an organic system bulking agent, and other inorganic system bulking agents, with the above-mentioned polycarbonate resin further in the range which does not spoil the purpose of this invention.

[0056] Especially the combination method of polycarbonate resin and inorganic conductivity material of having said specific physical-properties value is not specified, and can adopt the method usually used with this seed technology. The resin constituent of this invention obtained in this way has the outstanding mechanical property, thermal resistance, and conductivity, and is suitable as objects for manufacture, such as components, such as various kinds of electrical and electric equipment, electronic equipment, an optical instrument, and an automobile, and housing.

[0057]

[Example] Hereafter, although an example explains this invention, this invention is not limited to the following examples, unless the summary is exceeded.

The manufacturing method of polycarbonate resin is shown as an example of manufacture below manufacture of polycarbonate resin. In addition, analysis of the obtained polycarbonate resin was performed with the following measuring method.

[0058] (1) Viscosity average molecular weight (Mv)

Using the Ubbelohde's viscosimeter, 20-degree C limiting viscosity [eta] was measured among the methylene chloride, and viscosity average molecular weight (Mv) was calculated from the following formulas.

[0059]

[Equation 4]

[eta] =  $1.23 \times 10^{-4} \times (M_v)^{0.83}$  .... (5)

[0060] (2) Colorimetry was performed by the end OH radical content titanium tetrachloride / acetic-acid method (method given in Makromol.Chem.88 215 (1965)). Measured value displayed the weight of the end OH radical to polycarbonate resin weight per ppm.

(3) Molecular weight distribution (Mw/Mn)

It measured with gel permeation chromatography (GPC). HLC-8020 (TOSOH CORP. make) was used for the measuring device, the tetrahydrofuran was used for the eluate, it asked by polystyrene conversion, and Mw/Mn was computed.

[0061] (4) Dynamic viscoelasticity dynamic viscoelasticity was measured as follows. 120 degrees C dried for 5 hours, press forming of the polycarbonate resin of a sample was carried out to disc-like [ with a diameter / of 25mm /, and a thickness of 1.5mm ] at 250 degrees C, and the sample for measurement was obtained. Before measurement, 120 degrees C, reduced pressure drying of the sample was carried out, and measurement was presented with it for 4 hours. Viscoelasticity measuring instrument RDA-700 (REOMETO Rix Corp. make) was used, and it equipped with the fixture of a parallel plate mold with a diameter of 25mm, and was set as 250 degrees C which is measurement temperature among the nitrogen air current with which are satisfied of the proper conditions of this device. Measurement temperature was set up by measuring the temperature in oven. The sample for measurement dried after that was set to the device, and it measured after standing by carrying out angular velocity of ten rads/s, and rotation of 10% of distortion so that the whole sample might fully serve as laying temperature. It asked for loss tangent Tandelta and complex coefficient-of-viscosity eta\* (Pa-s) by this measurement.

[0062] According to example of manufacture 1 drawing 1, an example of the embodiment of a method which manufactures the polycarbonate resin of this invention is explained. Drawing 1 is flow sheet drawing having shown one example of the manufacture method of this invention. the inside of drawing, and 1 -- a DPC (diphenyl carbonate) tank and 2 -- an impeller and 3 -- a BPA (bisphenol A) hopper and 4 -- a and b -- a raw material mixing chamber and 5 -- for a pump and 8, as for program control equipment and 10, a catalyst flow control valve and 9 are [ a DPC flow control valve and 6 / a BPA flow control valve and 7 / a pump and 11 ] catalyst tanks. For a by-product exhaust pipe, 13a, and b and c, as for the Max blend aerofoil and 15, a vertical-type polymerization tank and 14 are [ 12 / a horizontal-type polymerization tank and 16 ] grid aerofoils among drawing. The diphenyl carbonate melt prepared at 120 degrees C under nitrogen-gas-atmosphere mind, The bisphenol A powder measured under nitrogen-gas-atmosphere mind and, respectively From a DPC tank (1), so that it may become a 197.1 mols [ /h ] (DPC/BPA mole ratio; 1.040) feed ratio from 205.0 mols [ h ] /and a BPA hopper (3) It measured with the weight feeder of a micro motion type flowmeter and a loss in wait method, and the raw material mixing chamber (4a) adjusted to 140 degrees C under nitrogen-gas-atmosphere mind was supplied continuously. Then, raw material mixed liquor was further supplied to the 1st vertical-type churning polymerization tank (13a) of capacity 100L continuously through the pump (7) at the raw material mixing chamber (4b). on the other hand, continuation supply was started for 2% of the weight of the cesium carbonate aqueous solution through the catalyst installation pipe by the flow rate of 1.6 mL/h (0.5micro mol the amount of setting catalysts : to one mol of BPA(s)) as supply initiation, simultaneously the catalyst of the above-mentioned mixture.

[0063] At this time, actual catalyst control of flow was program control equipment (9), from the BPA flow rate and the amount of setting catalysts which were detected by the BPA flow control valve (6), calculated the setting catalyst flow rate and was carried out by controlling the opening of a catalyst flow control valve (8) so that this value and the catalyst flow rate surveyed with the measuring device formed in the catalyst flow control valve (8) are in agreement. It kept oil-level level constant, controlling [ controlled the 1st vertical-type churning polymerization tank (13a) possessing the Max blend aerofoil (14) at 220 degrees C under ordinary pressure and nitrogen-gas-atmosphere mind, and ] the bulb opening prepared in polymer discharge Rhine of the bottom of the tank section so that mean flow time becomes in 60 minutes further. Continuation supply of the polymerization liquid discharged from the bottom of the tank was carried out serially succeedingly at the 2nd, the vertical-type churning polymerization tank (13b, 13c) of capacity 100L possessing the 3rd Max blend aerofoil, and the horizontal-type polymerization tank (15) of capacity 150L possessing the 4th grid aerofoil (16). As shown in the following table, conditioning of the reaction condition in the 2nd - the 4th polymerization tank was carried out, respectively so that it might become an elevated temperature, a high vacuum, and a low agitating speed with advance of a reaction.

[0064] -  
[A table 1]

	温度 (°C)	圧 力 (Pa)	攪拌速度 (rpm)
第2重合槽(13b)	220	$1.33 \times 10^4$	110
第3重合槽(13c)	240	$2.0 \times 10^5$	75
第4重合槽(15)	280	$6.67 \times 10$	10

[0065] Between reactions, the phenol which controlled oil-level level and carried out the byproduction in each polymerization tank was removed from the by-product exhaust pipe (12) so that the mean flow time of the 2nd - the 4th polymerization tank might become 60 minutes. Under the above conditions, it operated continuously for 1500 hours. In addition, with the melting condition, to polycarbonate resin weight, it was introduced into the biaxial extruder possessing a three-step vent-port, and the polycarbonate resin extracted from the polymer exhaust port of the 4th polymerization tank pars basilaris ossis occipitalis carried out 4.0 ppm (it is 4.4 time mol to amount of neutralization of catalyst) addition, and hydrogenation and after devolatilizing, it pelletized p-toluenesulfonic-acid butyl.

[0066] The viscosity average molecular weight (Mv) and the end OH radical contents of polycarbonate resin which were obtained were 21,500 and 500 ppm, respectively. Moreover, when the time amount the amount less than mol of  $0.06 \mu\text{mol}$  and of setting catalysts, and within  $0.1 \mu\text{mol}$  was computed to one mol of aromatic series dihydroxy compounds from the continuous measurement data (it is hereafter called for short "the continuous measurement data of a catalyst flow control valve".) of the catalyst flow rate surveyed with the measuring device formed in the catalyst flow control valve (8), they were 96.7% of all production time, and 99.1%, respectively. Molecular weight distribution (Mw/Mn) and the value of Tan delta/eta  $\approx 0.87$  were 2.3 and 4,850, respectively. This is expressed as PC-1.

[0067] In the example 1 of example of comparison manufacture 1 manufacture, program control equipment was not installed but the catalyst flow rate was carried out like the example 1 of manufacture except having fixed to 1.6 mL/h ( $0.5 \mu\text{mol}$  the amount of setting catalysts : to one mol of BPA(s)). The viscosity average molecular weight (Mv) and the end OH radical contents of polycarbonate resin which were obtained were 22,400 and 500 ppm, respectively. Moreover, when the time amount the amount less than mol of  $0.06 \mu\text{mol}$  and of setting catalysts, and within  $0.1 \mu\text{mol}$  was computed from the continuous measurement data of a catalyst flow control valve to one mol of aromatic series dihydroxy compounds, they were 89.9% of all production time, and 91.7%. Molecular weight distribution (Mw/Mn) and the value of Tan delta/eta  $\approx 0.87$  were 2.7 and 2,240, respectively. This is expressed as PC-2.

[0068] The polycondensation of the phosgene was carried out to example of comparison manufacture 2 bisphenol A by the interface method, and end closure was carried out with the phenol. The viscosity average molecular weight (Mv) and the end OH radical contents of polycarbonate resin which were obtained were 22,100 and 30 ppm, respectively. Molecular weight distribution (Mw/Mn) and the value of Tan delta/eta  $\approx 0.87$  were 2.3 and 7,550, respectively. This is expressed as PC-3.

[0069] By the combination formula shown in one to examples 1-3 and example of comparison 6 table -1, and table-2, polycarbonate resin and inorganic conductivity material were blended, and it kneaded and pelletized at the barrel temperature of 280 degrees C by single screw extruder VS-40 (product made from Tanabe Plastics). After drying 120 degrees C of obtained pellets for 5 hours, the Sumitomo Heavy Industries make, SAIKYAPPU M-2, and mold bundle force 75T are used Cylinder temperature: On conditions (300 degrees C and die-temperature:100 degree C), injection molding of various test pieces was performed and the result which does not have a line was shown for the following evaluation in table-1 and table-2 using the obtained shaping sample.

[0070] (5) Bending elastic modulus ISO The three-point bending test was performed according to the bending test method by 178.

(6) Heat deflection temperature ISO According to 75, the heat deflection temperature in 1.80MPa was measured.

(7) Conductivity (surface-electrical-resistance value)

The Sumitomo Heavy Industries make, SAIKYAPPU M-2, and mold bundle force 75T are used Cylinder temperature: The plate of 80mmx40mmx3.2mm was fabricated on conditions (300 degrees C and die-temperature:100 degree C), and the surface-electrical-resistance value was measured by Mitsubishi

Chemical RORESUTA or Polyester (RORESUTA was used about which becomes less than [ it ] using Huy Lester about a thing with a value of 104ohms or more).

[0071] (8) Antistatic engine performance (an electrification relative value and electrification half-life)

It measured about the electrification relative value and the electrification half-life using the plate of 40mmx80mmx3.2mmt. Static ONESUTO meter was used for the electrification relative value and the electrification half-life, and they performed it the condition for [ \*\*\*\* voltage / of 10kV /, and \*\*\*\* time amount ] 1 minute.

(9) The 40mm x80mmx3.2mmt plate of appearance of mold goods was observed visually, and it judged based on the following criteria.

O; fitness \*\*; [0072] with intense float of the x; inorganic conductivity material with which the float of inorganic conductivity material and the aggregate of inorganic conductivity material are seen a little and aggregate of inorganic conductivity material In addition, raw materials other than the polycarbonate resin used in an above-mentioned example and the above-mentioned example of a comparison are shown below.  
Carbon fiber: The Toho Rayon Co., Ltd. make, BESUFAITO HTA-C6-SR, the diameter of fiber of 7 micrometers, fiber length of 6mm.

Graphite: The Nippon Sheet Glass Co., Ltd. make, carbon flake #585, 340 meshes of average grain size.

Conductive carbon black: The LION make, KETCHIEN EC (oil absorption of 360ml / 100g).

Carbon nanotube: High peri-on international company make, PC/15BN (master pellet which consists of 15 % of the weight of carbon nanotubes, and 85 % of the weight of polycarbonate resin).

[0073]

[A table 2]

		表一			
		実施例			
		1	2	3	4
配 合	PC-1	重量部	100	100	100
	PC-2	重量部			
	PC-3	重量部			
	炭素繊維	重量部	30	10	
	グラファイト	重量部		10	
特 性	カーボンブラック	重量部			10
	カーボンナノチューブ	重量部			3
	粘度平均分子量		21,500	21,500	21,500
	分子量分布(Mw/Mn)		2.3	2.3	2.3
	$\tan \delta / \eta^{*-0.87}$		4850	4850	4850
特 性	末端水酸基濃度	ppm	500	500	500
	曲げ弾性率	MPa	13,800	7,850	2,350
	熱変形温度	°C	144	143	134
	表面抵抗値	$\Omega$	$3 \times 10^1$	$7 \times 10^1$	$5 \times 10^6$
	帯電相対値	mV	0.5	0.3	0.6
性	帯電半減期	sec	130	20	5
	成形品の外観		○	○	○

[0074]

[A table 3]

		表-2	比較例			
			1	2	3	4
配 合	PC-1	重量部				
	PC-2	重量部	100	100		
	PC-3	重量部			100	100
	炭素繊維	重量部	30	10		
	グラファイト	重量部		10		
	カーボンブラック	重量部			10	
特 性	カーボンナノチューブ	重量部				3
	粘度平均分子量		22,400	22,400	22,100	22,100
	分子量分布 (Mw/Mn)		2.7	2.7	2.3	2.3
	$\tan \delta / \eta \times 10^{-0.87}$		2240	2240	7550	7550
	末端水酸基濃度	ppm	500	500	30	30
	曲げ弾性率	MPa	12,800	7,500	2,330	2,340
	熱変形温度	°C	143	142	132	132
	表面抵抗値	$\Omega$	$1 \times 10^2$	$4 \times 10^2$	$6 \times 10^7$	$5 \times 10^7$
	帯電相対値	mV	0.7	0.5	0.8	0.2
	帯電半減期	sec	190	35	9	4
成形品の外観			×	×	×	×

[0075]

[Effect of the Invention] It excels in a mechanical strength or thermal resistance, and the appearance of the fluidity which was the conventional defect, or mold goods is improved by addition of inorganic conductivity material in the top where conductivity and antistatic nature are good, the polycarbonate resin constituent of this invention can be used for various industrial ways including camera components, or OA and electric electronic parts, and the meaning is large.

[Translation done.]



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TECHNICAL FIELD

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[A technical field to which invention belongs] This invention relates to a polycarbonate resin constituent which was excellent in a suitable mechanical strength and thermal resistance for housing, components, etc. of an electric electronic product, and dimensional stability, and was excellent in appearance of conductivity, antistatic nature, and mold goods in more detail about a polycarbonate resin constituent which comes to blend inorganic conductivity material.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art] Polycarbonate resin is broadly used in many fields as resin excellent in a mechanical strength, thermal resistance, transparency, dimensional stability, etc. Especially, the cases used for electric electronic parts have been increasing in number very much by development of the information industry in recent years. However, since it is the insulation which originally does not conduct the electrical and electric equipment, the synthetic resin containing polycarbonate resin cannot be used for the components of which conductivity is required if it remains as it is. Moreover, there is difficulty also in using it for the electric electronic parts which dust and dust tend to adhere and dislike adhesion of dust and dust, since synthetic resin tends to be charged. As this cure, conductive material is blended with polycarbonate resin and giving conductivity and antistatic nature is performed. The polycarbonate resin which carbon fiber metallurgy group fiber and conductive carbon black were mentioned, and blended these as typical conductive material is widely used in the industrial field as which conductivity and antistatic nature including electric electronic parts are required.

[0003] However, in order to give conductivity to the polycarbonate resin which is originally insulation, it is necessary to blend most quantity of conductive material, therefore the mechanical strength, the thermal resistance, the dimensional stability, and the moldability (fluidity) of polycarbonate resin original fall, and the problem that mold-goods appearance is spoiled arises. Moreover, in recent years, the thinning of components and lightweight-ization progress, conductivity is discovered in a smaller amount, and the polycarbonate resin which suppressed the fall of a fluidity or a mechanical strength is called for. On the other hand, for example, invention concerning the constituent which blended the carbon fiber with the polycarbonate resin which has the hydroxyl group of a specific rate in a resin end is indicated by JP,2001-49109,A. However, the adhesion of polycarbonate resin and a carbon fiber was improved, the chief aim has set to raise a mechanical strength, and this invention of the conductive amelioration effect is insufficient. Moreover, it is indicated by JP,1-21185,B by blending phosphorus compounds with the constituent which consists of polycarbonate resin and a carbon fiber that conductivity improves. Although conductivity is improving by adding this component to be sure, the thermal resistance which polycarbonate resin originally has is spoiled, or we are anxious about generating of the mold deposit by combination of a low-molecular object etc.

[0004] Furthermore, although it will be difficult to give conductivity about the case where it is blended with polycarbonate resin, the conductive material, for example, the conductive carbon black, other than a carbon fiber, with a mechanical strength and thermal resistance held and the aggregate accompanying the maldistribution of carbon black will occur, it is in the condition which what knowledge does not have, either about such amelioration technique. The polycarbonate resin constituent excellent in the appearance of conductivity, antistatic nature, and mold goods was called for under this condition, without spoiling the mechanical strength of polycarbonate resin original, thermal resistance, and dimensional stability in any way.

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[Translation done.]

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EFFECT OF THE INVENTION

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[Effect of the Invention] It excels in a mechanical strength or thermal resistance, and the appearance of the fluidity which was the conventional defect, or mold goods is improved by addition of inorganic conductivity material in the top where conductivity and antistatic nature are good, the polycarbonate resin constituent of this invention can be used for various industrial ways including camera components, or OA and electric electronic parts, and the meaning is large.

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[Translation done.]

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention offers the polycarbonate resin constituent excellent in the appearance of conductivity, antistatic nature, and mold goods, without spoiling the mechanical strength of polycarbonate resin original, thermal resistance, and dimensional stability in any way.

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[Translation done.]

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MEANS

[Means for Solving the Problem] As a result of repeating examination wholeheartedly that said technical problem should be solved, this invention persons to a surprising thing A resin constituent which blended inorganic conductivity material with polycarbonate resin which is obtained by specific process and has specific melting viscoelasticity Distribution of inorganic conductivity material came to complete a header and this invention for it being very good and excelling in appearance of conductivity and mold goods, without sacrificing a mechanical strength and thermal resistance compared with polycarbonate resin which has the property of an and also [ molecular weight is an EQC substantially ]. That is, a summary of this invention is a resin constituent which carries out 0.1-100 weight section content of the inorganic conductivity material to the polycarbonate resin 100 weight section, and the loss angle delta which this polycarbonate resin was manufactured with scorification, and was measured on conditions with a temperature [ of 250 degrees C ] and an angular velocity of ten rads [ /s ], and complex coefficient-of-viscosity  $\eta^*$  (Pa-s) consist in a polycarbonate resin constituent characterized by filling the following relational expression (1).

[0007]

[Equation 2]

$$2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000 \dots (1)$$

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained concretely. It is required for the loss angle delta measured on conditions with a temperature [ of 250 degrees C ] and an angular velocity of ten rads [ /s ] and complex coefficient-of-viscosity  $\eta^*$  (Pa-s) to fill the following relational expression (1), it is the range of the following relational expression (2) preferably, and the polycarbonate resin used for this invention constituent is the range of the following relational expression (3) still more preferably. this invention -- setting -- this -- the value of  $\tan \delta / \eta^* - 0.87$  was used as a parameter which shows the melting viscoelasticity of polycarbonate resin. When the value of  $\tan \delta / \eta^* - 0.87$  exceeds the case of less than 2500, or 6000, the maldistribution of inorganic conductivity material occurs, and the appearance of a fluidity, conductivity, and mold goods is spoiled.

[0009]

[Equation 3]

$$2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000 \dots (1)$$

$$2800 \leq \tan \delta / \eta^* - 0.87 \leq 5500 \dots (2)$$

$$3000 \leq \tan \delta / \eta^* - 0.87 \leq 5000 \dots (3)$$

[0010] Generally the loss angle delta is known as one of the indexes which expresses the delay of the phase of the strain over stress searched for from measurement of dynamic melting viscoelasticity, and expresses a dynamic viscoelasticity action. delta ( $\tan \delta$ ) shows that the viscosity-property of viscoelasticity is strong when the value is large, and when small, it shows that an elastic property is strong. The factor which determines this value is complicated, for example, the molecular structure including branching structures, such as a class of polycarbonate resin manufacture raw material (monomer including copolymerization), a copolymerization presentation, structure of a copolymer, and the number of the branch points, the length of branched chain, etc., molecular weight, molecular weight distribution, etc. are mentioned.

[0011] According to examination of this invention persons, the polycarbonate resin manufactured by the interface method using the conventional phosgene had the problem that get worse extremely, and inorganic conductivity material came up to the mold-goods surface, or a fluidity condensed further at the time of

injection molding, and spoil the appearance of mold goods, when inorganic conductivity material was added. If the polycarbonate resin manufactured by such interface method plots the value of  $\delta$  (Tandelta) to the logarithmic coordinates to the complex coefficient of viscosity ( $\eta^*$  (Pa-s)) which is indexes, such as molecular weight, --  $\tan \delta / \eta^* - 0.87 =$  -- it turned out that it stands in a line mostly on the straight line of about 8000. (Here,  $-0.87$  which is the characteristic of  $\eta^*$  expresses the above-mentioned slope of a line, and  $\tan \delta / \eta^* - 0.87$  express the value of Tandelta when extrapolating the above-mentioned straight line to  $\eta^* = 1$  (Pa-s).) That is, it becomes possible to eliminate the molecular weight (viscosity) dependency of a loss angle by using the value of  $\tan \delta / \eta^* - 0.87$  for a parameter. .

[0012] On the other hand, the polycarbonate resin which has that the polycarbonate resin manufactured by scorification generally does not ride on this straight line and scorification polycarbonate resin in the range of  $2500 \leq \tan \delta / \eta^* - 0.87 \leq 6000$  although mold-goods appearance is [ that a flow pattern tends to come out of the thing of  $\tan \delta / \eta^* - 0.87 < 2500$  at the time of injection molding ] inferior found out that the appearance of a fluidity and mold goods was excellent also in the range where molecular weight is large.

[0013] the stress with which the one where the value of  $\delta$  (Tandelta) is smaller pushes polycarbonate resin against the mold-goods surface by it by the normal stress of polycarbonate resin becoming large as an effect which the polycarbonate resin specified with this melting viscoelasticity parameter gives to a fluidity in this invention -- high -- consequently, condensation and the mold-goods surface of inorganic conductivity material -- it looms and it is presumed that  $\eta^*$  decreases remarkably. Moreover, in addition to this, the fluidity for a thin-walled part becomes high, and it is effective in a moldability being improved. However, when the value of  $\delta$  (Tandelta) is too small, if certain, although there is nothing, a flow pattern occurs on the mold-goods surface, and a reason is not desirable.

[0014] In addition, in this invention, although what could also add various stabilizers, the ultraviolet ray absorbent, the release agent, the coloring agent, etc. to polycarbonate resin, may add these additives before pellet manufacture in the middle of manufacture of polycarbonate resin, and generally contained those additives may be called "polycarbonate resin", the value of the above-mentioned relational expression specified by this invention is calculated about the polycarbonate resin which does not contain these additives at all.

[0015] It is desirable that it is 50-1000 ppm, as for the end OH radical content of the polycarbonate resin used for this invention, it is still more desirable that it is 70-800 ppm, and it divides and is desirable that it is 90-600 ppm. When an end OH radical content exceeds 1000 ppm, thermal stability and hydrolysis-proof nature get worse, and when too few, there is orientation for manufacture of the polycarbonate resin of desired molecular weight to become difficult.

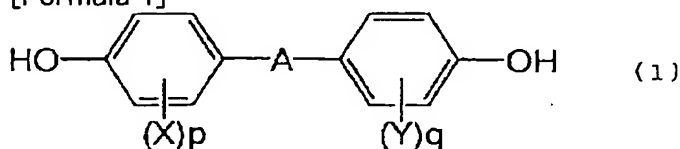
[0016] When the molecular weight of polycarbonate resin is low, although excelled in a fluidity, it is inferior to a mechanical strength. On the contrary, when the molecular weight of polycarbonate resin is high, although excelled in a mechanical strength, it is inferior to a fluidity. In this invention, the polycarbonate resin of 12,000-30,000 has desirable viscosity average molecular weight, the polycarbonate resin of 14,000-26,000 has still more desirable viscosity average molecular weight, and the polycarbonate resin of 16,000-24,000 has the most desirable viscosity average molecular weight.

[0017] The polycarbonate resin concerning this invention is manufactured by scorification, and if it is resin which has the rate of viscoelasticity which fills the above-mentioned formula (1), although especially the process is not limited, an aromatic series dihydroxy compound and carbonic acid diester can be manufactured as a raw material, for example as following.

[0018] Aromatic series dihydroxy compound: The aromatic series dihydroxy compound which is one of the raw materials of the polycarbonate resin of this invention is shown by the following formula (1).

[0019]

[Formula 1]



[0020] (A is a divalent radical shown by the shape of single bond and a straight chain of the carbon numbers 1-10 which may be replaced, the letter of branching, an annular divalent hydrocarbon group or -O-, -S-, -CO-, or -SO<sub>2</sub>- among a formula (1), X and Y are the hydrocarbon groups of a halogen atom or

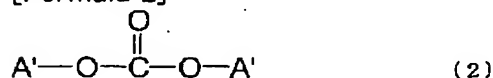
carbon numbers 1-6, and the integer of p and 0, or 1.) In addition, and p and q may be the same, or may differ from each other mutually, respectively.

[0021] As a typical aromatic series dihydroxy compound For example, screw (4-hydroxyphenyl) methane, 2, and 2-screw (4-hydroxyphenyl) propane, 2 and 2-screw (4-hydroxy-3-methylphenyl) propane, 2, and 2-screw (4-hydroxy-3-t-butylphenyl) propane, 2 and 2-screw (4-hydroxy-3,5-dimethylphenyl) propane, 2 and 2-screw (4-hydroxy-3,5-dibromo phenyl) propane, 4 and 4-screw (4-hydroxyphenyl) heptane, 1, and 1-screw (4-hydroxyphenyl) cyclohexane, 4, a 4'-dihydroxy biphenyl, 3, 3', 5, 5'-tetramethyl-4,4'-dihydroxy biphenyl, A screw (4-hydroxyphenyl) sulfone, a screw (4-hydroxyphenyl) sulfide, the screw (4-hydroxyphenyl) ether, a screw (4-hydroxyphenyl) ketone, etc. are mentioned. These aromatic series dihydroxy compounds are independent, or two or more sorts can be mixed and used for them. Also in these, 2 and 2-screw (4-hydroxyphenyl) propane (hereafter, it may also be called "bisphenol A" and may be written as "BPA") is desirable.

[0022] Carbonic acid diester: The carbonic acid diester which is other one of the raw materials is shown by the following formula (2).

[0023]

[Formula 2]



[0024] (A' is the shape of a straight chain, the letter of branching, or the annular univalent hydrocarbon group of the carbon numbers 1-10 which may be replaced among a formula (2), and two A' may be the same or may differ mutually.) The dialkyl carbonate represented by the substitute diphenyl carbonate represented by diphenyl carbonate, JITORIRU carbonate, etc., dimethyl carbonate, diethyl carbonate, G t-butyl carbonate, etc. as typical carbonic acid diester, for example is mentioned. These carbonic acid diester is independent, or two or more sorts can be mixed and used for it. Also in these, diphenyl carbonate (it may be hereafter written as "DPC") and substitute diphenyl carbonate are desirable.

[0025] Moreover, the above-mentioned carbonic acid diester may replace the amount not more than 30 mol % with dicarboxylic acid or dicarboxylic acid ester preferably [ it is desirable and ] to the 50 mol % less or equal and a pan. As typical dicarboxylic acid or dicarboxylic acid ester, a terephthalic acid, isophthalic acid, terephthalic-acid diphenyl, isophthalic acid diphenyl, etc. are mentioned. Polyester carbonate is obtained when it replaces with such dicarboxylic acid or dicarboxylic acid ester. These carbonic acid diester (the ester of the dicarboxylic acid which the above replaced, or dicarboxylic acid is included.) It is below the same. It is usually superfluously used to an aromatic series dihydroxy compound. namely, an aromatic series dihydroxy compound -- receiving -- a mole ratio -- 1.001-1.3 -- it is preferably used within the limits of 1.01-1.2. Although the end OH radical of polycarbonate resin will decrease if the end OH radical of the polycarbonate resin manufactured when the mole ratio became smaller than 1.001 increases, and thermal stability and hydrolysis-proof nature get worse and a mole ratio becomes large from 1.3, the speed of an ester exchange reaction falls and there is orientation for manufacture of the polycarbonate resin of desired molecular weight to become difficult under the same conditions. In this invention, it is good to use the polycarbonate resin adjusted to the range whose end OH radical content is 50-1000 ppm.

[0026] As the supply method of the raw material to a raw material mixing chamber, in order that the direction of a liquid condition may tend to maintain measuring precision highly, it is desirable to carry out melting of one side or both, and to supply them in the state of a liquid among an aromatic series dihydroxy compound and carbonic acid diester. When supplying a raw material in the state of a liquid, as a metering installation, an oval flow meter, a micro motion type flowmeter, etc. can be used. When supplying a raw material by the solid state, it is desirable to use what measures weight, and although weight feeders, such as a \*\* RUTO type and a loss in wait type, can be used, especially a loss in wait method is on the other hand, more desirable than what measures capacity like a screw-type feeder.

[0027] Ester interchange catalyst: In case polycarbonate resin is manufactured with scorification, a catalyst is usually used. In the method of manufacturing the polycarbonate resin concerning this invention, although there is no limit in a catalyst kind, generally basic compounds, such as an alkali metal compound, an alkaline-earth-metal compound, a basic boron compound, basic phosphorus compounds, a basic ammonium compound, or an amine system compound, are used. These may be used by one kind and may be used combining two or more kinds.



[0028] the amount of the catalyst used -- one mol of aromatic series dihydroxy compounds -- receiving -- 0.05-5micro mol -- desirable -- 0.08-4micro mol -- it is used within the limits of 0.1-2micro mol still more preferably. Polymerization activity required to manufacture the polycarbonate resin of desired molecular weight if there is less amount of the catalyst used than the amount of above is not acquired, but when [ than this amount ] more, a polymer hue gets worse, and branching-ization of polymer also progresses, and there is orientation for the fluidity at the time of shaping to fall.

[0029] As an alkali metal compound, there are organoalkali metal compounds, such as inorganic alkali metal compounds, such as a lithium, sodium, a potassium, a rubidium, a hydroxide of caesium, a carbonate, and carbonic acid hydride, an alcoholate, a phenolate, and organic carboxylate, etc. Also in these alkali metal compounds, a caesium compound is desirable, and if the concrete most desirable caesium compound is mentioned, they will be cesium carbonate, carbonic acid hydrogen caesium, and cesium hydroxide.

[0030] Moreover, as an alkaline earth metal compound, there are organoalkaline earth metal compounds, such as inorganic alkaline earth metal compounds, such as beryllium, magnesium, calcium, strontium, a hydroxide of barium, and a carbonate, an alcoholate, a phenolate, and organic carboxylate, etc.

[0031] As a basic boron compound, for example Tetramethyl boron, tetraethyl boron, Tetra-propyl boron, tetrabutyl boron, trimethyl ethyl boron, Trimethyl benzyl boron, trimethyl phenyl boron, triethyl methyl boron, Triethyl benzyl boron, triethyl phenyl boron, tributyl benzyl boron, Tributyl phenyl boron, tetra-phenyl boron, benzyl triphenyl boron, Sodium salt, such as methyl triphenyl boron and butyl triphenyl boron, potassium salt, lithium salt, a calcium salt, magnesium salt, barium salt, or a strontium salt is mentioned.

[0032] As basic phosphorus compounds, the 4th class phosphonium salt guided from trivalent phosphorus compounds, such as a triethyl phosphine, a tree n-propyl phosphine, a tree i-propyl phosphine, tri-n-butyl phosphine, triphenyl phosphine, and tributyl phosphine, or these compounds is mentioned, for example.

[0033] As a basic ammonium compound, for example Tetramethylammonium hydroxide, Tetraethylammonium hydroxide, tetrapropylammonium hydroxide, Tetrabutylammonium hydroxide, trimethyl ethylammonium hydroxide, Trimethyl benzyl ammonium hydroxide, trimethyl phenyl ammonium hydroxide, Triethyl methylammonium hydroxide, triethyl benzyl ammonium hydroxide, Triethyl phenyl ammonium hydroxide, tributyl benzyl ammonium hydroxide, Tributyl phenyl ammonium hydroxide, tetra-phenyl ammonium hydroxide, Benzyl triphenyl ammonium hydroxide, methyl triphenyl ammonium hydroxide, butyl triphenyl ammonium hydroxide, etc. are mentioned.

[0034] As an amine system compound, 4-aminopyridine, 2-aminopyridine, N, and N-dimethyl-4-aminopyridine, 4-diethylamino pyridine, 2-hydroxypyridine, 2-methoxy pyridine, 4-methoxy pyridine, 2-dimethylamino imidazole, 2-methoxy imidazole, an imidazole, 2-mercaptoimidazole, 2-methylimidazole, an amino quinoline, etc. are mentioned, for example. An alkali metal compound is desirable practical among these catalysts.

[0035] The above-mentioned ester interchange catalyst is used with the gestalt of the catalyst solution which dissolved in the solvent. As a solvent, the solvent which dissolves a raw material aromatic series dihydroxy compound besides water, an acetone, alcohol, toluene, and a phenol and coal-for-coke-making acid diester is mentioned, for example. In these, water is desirable, and when making especially an alkali metal compound into a catalyst, considering as an aqueous solution is suitable.

[0036] The manufacture method of polycarbonate resin: Although it will not be especially limited if the method of manufacturing polycarbonate resin from an aromatic series dihydroxy compound and carbonic acid diester is scorification and it is the method by which the polycarbonate resin which has said specific physical properties is obtained, the following methods are adopted, for example. That is, by a raw material mixing chamber etc., after agitating both raw materials to homogeneity, a catalyst is added, a polymerization is performed and polycarbonate resin is usually produced. For example, it is desirable to supply continuously the above-mentioned aromatic series dihydroxy compound and both the raw materials of carbonic acid diester to a raw material mixing chamber, and to supply the obtained mixture and an ester interchange catalyst to a polymerization tank continuously. In order to be stabilized and to produce the polycarbonate resin of the above-mentioned specific physical properties of this invention in that case, the method of satisfying the following (a) and both the conditions of (b) at least is adopted, for example.

[0037] (a) Choose from within the limits of 0.05 - 5micro mol the "amount of setting catalysts" which is the aim catalyst amount of supply for keeping constant the amount of catalysts to the aromatic series dihydroxy compound or one mol of carbonic acid diester supplied to a polymerization tank for every unit production time which carried out fractionation of all the production time to one or more to one mol of aromatic series dihydroxy compounds. In addition, with "all production time", it corresponds to the feeding

time amount which produces polycarbonate resin stably in a polymerization tank, and the polycarbonate resin production time at the time of the instabilities at the time of manufacture termination etc. does not contain at the time of starting and a grade change.

(b) The actual amount of ester interchange catalysts (only henceforth "the actual amount of catalysts") to which at least 95% of time amount of each unit production time is supplied is maintained to one mol of aromatic series dihydroxy compounds by the value within each the amount mol of  $0.1 \mu\text{mol}$  of setting catalysts. In the above (a), through all production time, it is not necessary to be necessarily constant value, fractionation of all the production time is carried out to one or more, and the amount of setting catalysts can be set up for every unit production time of the.

[0038] Hereafter, when this method is explained in detail and all production time is the unit production time of single fractionation, as for at least 95% of that time amount, the actual amount of catalysts is maintained to one mol of aromatic series dihydroxy compounds to the value within the amount mol of  $0.1 \mu\text{mol}$  of setting catalysts. Moreover, when fractionation of all the production time is carried out to two or more unit production time and the amount of setting catalysts is changed, at least 95% of time amount of each unit production time maintains the actual amount of catalysts to the value within each the amount mol of  $0.1 \mu\text{mol}$  of setting catalysts. In any case, it is desirable to maintain within the amount mol of  $0.08 \mu\text{mol}$  of setting catalysts, and it is desirable. [ of especially the thing to maintain within the amount mol of  $0.06 \mu\text{mol}$  of setting catalysts ] Furthermore, the rate of time amount that the actual amount of catalysts is maintained by the controlled value is more desirable so that it is close to 100%, although what is necessary is just all production time or at least 95% of each unit production time. If it becomes time amount fewer than 95%, the polycarbonate resin of desired molecular weight and an end OH radical content will no longer be obtained. When there are many rates of time amount especially with more amounts of catalysts than the amount of setup, the polycarbonate resin hue acquired gets worse, and it carries out that branching-ization of polycarbonate resin progresses etc., and there is orientation for the fluidity when what satisfies the relational expression specified by this invention as a result no longer being obtained, and fabricating this polycarbonate resin to also fall. In addition, although it is possible to manufacture the polycarbonate resin of this invention even if it changes the manufacture conditions of polymerization reaction time, such as whenever [ polymerization temperature polymerization time amount, and reduced pressure ], it is thought that stable production becomes difficult. It turned out that the actual amount of catalysts is maintained within the amount mol of  $0.1 \mu\text{mol}$  of setting catalysts, and a very small fluctuation range, the specific relational expression specified by this invention is satisfied, without needing complicated polymerization actuation for the first time by continuing supply, and polycarbonate resin excellent in many physical properties, such as narrow molecular weight distribution, a color tone, a fluidity, thermal resistance, and machine physical properties, can be stably produced now.

[0039] It is desirable to use an oval flow meter, a micro motion type flowmeter, etc., and to measure and supply the catalyst flow rate which supplies it to a polymerization tank in order to make the value within the amount mol of  $0.1 \mu\text{mol}$  of setting catalysts maintain the aforementioned actual amount of catalysts. In order to control catalyst supply automatically, the setting catalyst flow rate first computed from the amount of supply to the raw material preparation tub of the amount of setting catalysts, the aromatic series dihydroxy compound, or carbonic acid diester which inputted and mentioned above the measured value of a continuously actual catalyst flow rate to the computer is measured. When the measured value of an actual catalyst flow rate differs from this setting catalyst flow rate in that case, this result is told to catalyst measuring and a feeder, and the opening of a bulb etc. is adjusted, and it controls so that an actual catalyst flow rate and a setting catalyst flow rate are in agreement.

[0040] If rationalization of the time between measurements of an actual catalyst flow rate is considered enough, it is possible to control like [ the control based on continuous intermittent measurement ] continuous measurement, but in order to obtain the product of the stable quality, as for the automatic control of catalyst supply here, it is desirable that it is continuous automatical measurement. That is, if a catalyst flow rate can be measured automatically continuously, since become possible to control quickly and continuously the catalyst amount of supply to a polymerization tank, consequently it is maintained by the fixed setting catalyst flow rate, and deflection, such as viscosity average molecular weight of polycarbonate resin and an end OH radical content, is small, and molecular weight distribution become narrow and a product with many still more uniform physical properties, such as a color tone, a fluidity, thermal resistance, and machine physical properties, is obtained, it is desirable. In the unit production time of a certain amount of setting catalysts, it can be easily judged [ how much / the actual amount of

catalysts ] from the measurement result by the above-mentioned measurement means to the value within the amount mol of  $\leq 0.1$  micro of setting catalysts whether time amount existence was recognized. In continuous measurement, it is judged by finding the accumulation time amount which is within the amount mol of  $\leq 0.1$  micro of catalysts beforehand set up from the curve which shows the relation between an actual raw material mole ratio and the measuring time, and the accumulation time amount which shifted rather than  $\leq 0.1$  micro mol whether at least 95% of time amount of the unit production time in this amount of setting catalysts was maintained by the value within  $\leq 0.1$  micro mol. If it is continuous measurement even when it is not continuous measurement, it can judge by the method of carrying out statistics processing of this etc.

[0041] The reaction of two or more steps (ester exchange reaction) of polymerization reactions of polycarbonate resin in two or more polymerization tanks, i.e., usually carry out continuously at 3-7 steps of multistage production processes, is desirable. As a concrete reaction condition, it considers as the range for temperature: 150-320 degree C, pressure: ordinary pressure -2Pa, and mean-flow-time: 5 - 150 minutes, and in order to make more effective discharge of a phenol which carries out a byproduction with advance of a reaction in each polymerization tank, it is gradually set more as an elevated temperature and a twist high vacuum within the above-mentioned reaction condition. In order to prevent debasement, such as a hue of the polycarbonate resin obtained, a setup of low temperature and the shortest possible residence time is desirable as much as possible. In addition, as for the automatic control of the actual amount of catalysts in the case of using two or more polymerization tanks at a multistage production process, it is desirable to control the amount of supply of a catalyst automatically continuously, and it needs to have completed measurement and control less than to 1/3 of the residence time of the 1st polymerization tank in that case.

[0042] the equipment used in the above-mentioned ester exchange reaction -- a vertical type, a juxtaductal type, or a column -- you may be which format of type and a horizontal type. Usually, a turbine blade, a paddle aerofoil, a support aerofoil, a full zone aerofoil (Shinko Pantec Co., Ltd. make), The Sun Moeller aerofoil (Mitsubishi Heavy Industries, Ltd. make), the Max blend aerofoil (Sumitomo Heavy Industries, Ltd. make), One or more vertical-type polymerization tanks possessing a helical ribbon aerofoil, a torsion grid aerofoil (Hitachi Make), etc. are followed. A polymerization tank horizontal-type 1 shaft type [ , such as a disk mold and a cage mold, ], HVR and SCR, N-SCR (Mitsubishi Heavy Industries, Ltd. make), A BAIBO rack (Sumitomo Heavy Industries, Ltd. make), a glasses aerofoil, a grid aerofoil (Hitachi Make), Or the horizontal-type 2 shaft type polymerization tank possessing what combined the aerofoil which gave the feed function of a glasses aerofoil and polymer, for example, the aerofoil and/or inclination containing torsion, a twist, etc. attach can be used.

[0043] In the polycarbonate resin manufactured by the above-mentioned method, low molecular weight compounds which carry out a byproduction by the raw material monomer, the catalyst, and the ester exchange reaction, such as an aromatic series hydroxy compound and polycarbonate resin oligomer, usually remain. Especially, there are many amounts of residuals, and since a raw material monomer and an aromatic series hydroxy compound have a bad influence on physical properties, such as heat-resistant aging nature and hydrolysis-proof nature, it is desirable [ a hydroxy compound ] to be removed on the occasion of commercial production. There is no method of removing them, for example, it may devolatilize especially a limit continuously with a vent-type extruder. In that case, by adding an acid compound or its precursor and carrying out deactivation of the basic ester curing catalyst which remains in resin beforehand, the side reaction under devolatilization can be suppressed and a raw material monomer and an aromatic series hydroxy compound can be removed efficiently.

[0044] There is especially no limit in the acid compound to add or its precursor, and all can be used if there is an effect which neutralizes the basic ester curing catalyst used for a polycondensation reaction. Specifically A hydrochloric acid, a nitric acid, a boric acid, a sulfuric acid, a sulfurous acid, a phosphoric acid, phosphorous acid, Hypophosphorous acid, polyphosphoric acid, an adipic acid, an ascorbic acid, an aspartic acid, An azelaic acid, adenosine phosphate, a benzoic acid, a formic acid, a valeric acid, a citric acid, A glycolic acid, glutamic acid, a glutaric acid, a cinnamic acid, a succinic acid, an acetic acid, A tartaric acid, oxalic acid, p-toluene sulfinic acid, p-toluenesulfonic acid, Broensted acid and its ester, such as a naphthalene sulfonic acid, a nicotinic acid, a picric acid, picolinic acid, a phthalic acid, a terephthalic acid, a propionic acid, benzenesulfinic acid, benzenesulfonic acid, a malonic acid, and a maleic acid, are mentioned. These may be used independently or may be used combining two or more sorts. P-toluenesulfonic-acid methyl, a sulfonic-acid compound, or the ester compound, for example, p-toluenesulfonic acid, especially

p-toluenesulfonic-acid but etc. are desirable among these acid compounds or the precursor of those. [0045] the amount of neutralization of the basic ester curing catalyst which used the addition of these acid compounds or the precursor of those for the polycondensation reaction -- receiving -- a 0.1 to 50 time mol -- it adds in the range of a mol 0.5 to 30 times preferably. As a stage to add an acid compound or its precursor, as long as it is after a polycondensation reaction, it may be good at any time and which methods, such as a method which there is nothing and is directly added according to the description of an acid compound or its precursor or desired conditions, the method of dissolving in a suitable solvent and adding, and the method of using the masterbatch of the shape of a pellet or a flake, may be used for a limit special also to the addition method. A monopodium or two shafts are sufficient as the extruder used for devolatilization. Moreover, as a twin screw extruder, it may be an engagement mold twin screw extruder, and this direction rotation or the different direction rotation is sufficient as a hand of cut. For the purpose of devolatilization, what has the vent section after the acid compound addition section is desirable. Although there is no limit in the number of vents, two to ten steps of multistage vents are usually used. Moreover, in this extruder, if needed, additives, such as a stabilizer, an ultraviolet ray absorbent, a release agent, and a coloring agent, can be added, and it can also knead with resin.

[0046] As inorganic conductivity material blended with the polycarbonate resin constituent of this invention, the well-known inorganic conductivity material blended with thermoplastics can usually be used. If an example is given, the compound conductivity material which carried out the coat of the metal will be mentioned to the surface of the inorganic conductivity material of metal systems, such as conductive material of carbon systems, such as carbon black, a carbon fiber, graphite, a carbon whisker, and a carbon nanotube, a metal fiber, metal powder, and a metallic oxide, a carbon fiber, or a whisker and a glass fiber. Also in these, a carbon fiber, a metal fiber, metal powder, conductive carbon black, a carbon nanotube, and graphite are desirable, and these can use together independent or two sorts or more.

[0047] What was generally manufactured by baking as a carbon fiber used by this invention by using an acrylic fiber, petroleum or a carbon system special pitch, cellulose fiber, a lignin, etc. as a raw material is mentioned, and a base material is not asked especially although there is a thing of various types, such as quality of fire resistance, carbonaceous, or graphite. Furthermore, in order to improve the conductivity of a carbon fiber, the carbon fiber which carried out the metal coat on the surface of the carbon fiber may be used. The metals used for the surface coat of a carbon fiber are one or more sorts of metals, such as copper, nickel, silver, cobalt, aluminum, and iron, and the method of a metal coat has well-known vacuum deposition, well-known plating, etc. The average of the aspect ratio (fiber length/diameter of fiber) of a carbon fiber is ten or more preferably. Conductivity, and reinforcement and rigidity fall that the average of an aspect ratio is less than ten. The average of the aspect ratio (fiber length/diameter of fiber) of a carbon fiber is 50 or more more preferably. since the path of a carbon fiber is 3-15 micrometers, in order to adjust it to such an aspect ratio generally -- anything of configurations, such as a chopped strand, a roving strand, and a milled fiber, -- it can be used -- one sort -- or two or more sorts can be mixed and it can also use. Since the surface of a carbon fiber increases compatibility with resin unless the property of the constituent of this invention is spoiled, surface treatment, for example, silanizing, epoxy processing, urethane processing, oxidation treatment, etc. may be performed. As such a carbon fiber, it is marketed from Mitsubishi Chemical, Inc., for example by the trade name of BESUFAITO in a diamond lead and Toho Rayon Co., Ltd.

[0048] the graphite used for this invention constituent -- a natural scale-like graphite, a natural earthy graphite, an artificial graphite, etc. -- it is -- them -- one sort -- or two or more sorts can use it, mixing. As for the mean particle diameter of a graphite, what a 5-100-micrometer thing is desirable, and is 5-80 micrometers in a weighted mean is still more desirable, and its 5-60-micrometer thing is the most desirable. The eat lump by the screw worsens and a graphite with a mean particle diameter of less than 5 micrometers does not have it in measuring instability, when carrying out melting kneading using an extruder etc. [ desirable ] If mean particle diameter exceeds 100 micrometers, the appearance and dispersibility of mold goods are inferior and it is not desirable. As commercial graphite, carbon flake #585 of Nippon Sheet Glass Co., Ltd., CP of Japanese Graphite, CPB, CPB3 of China-Vietnam Graphite, CPB-30, and CPB-3000 grade are mentioned.

[0049] The conductive carbon black used for this invention constituent has desirable DBP (dibutyl phthalate) oil absorption of 100ml of 2414 to ASTM-D88 convention / thing 100g or more. If DBP oil absorption uses carbon black (100ml / less than 100g), the rate of addition of the carbon black for giving antistatic nature causes [ become high and ] the fall of a fluidity or a mechanical strength and is not

desirable. as commercial conductive carbon black -- the diamond black (turnip black) of Mitsubishi Chemical, Inc., and DIN of Electrochemistry -- a turnip -- there is the Balkan Peninsula C of a rack (acetylene black), KETCHIEN black 600JD of LION, Inc., and Cabot Corp. etc.

[0050] What was manufactured from copper, brass, zinc, stainless steel, aluminum, nickel, magnesium, iron, gold, and silver can be used for the metal fiber used by this invention by the coil strip cutting method, the wire drawing drawing method, the melt spinning method, and the wire cutting method. 3-100 micrometers of diameters of a metal fiber are 5-50 micrometers preferably, and number mean fiber length is 0.3-3mm preferably 0.1-5mm.

[0051] The metal powder used by this invention can use what was manufactured from copper, brass, zinc, stainless steel, ALUMINIUM, nickel, magnesium, iron, gold, and silver. The mean particle diameter of a metal powder has desirable 0.5-20 micrometers, and since impact strength will fall and a fluidity will fall in less than 0.5 micrometers if 20 micrometers is exceeded, it is not desirable. Surface treatment may be carried out also to the metal fiber and metal powder which are used by this invention by for example, the silane system coupling agent or the titanate system coupling agent, and you may use.

[0052] It is carbon fibril which has hollow structure, as for the carbon nanotube used by this invention, it is desirable that they are the outer diameter of 3.5-70nm and five or more aspect ratios, and especially its thing that are the outer diameter of 4-60nm and ten or more aspect ratios is desirable. The conductivity of the resin constituent which will be obtained if a fibril outer diameter is inferior to the dispersibility to the inside of resin in a less than 3.5nm object and exceeds 70nm is dissatisfied. Moreover, the conductivity of the resin constituent with which an aspect ratio is obtained less than by five is dissatisfied.

[0053] A carbon nanotube is cylinder-like fibril at the essential target with which it has the outside field which essentially consists of a continuous a large number layer and internal hollow field of the carbon atom arranged regularly, and each class and a hollow field are substantially arranged around the cylinder shaft of this fibril at this heart. Furthermore, the carbon atom arranged regularly [ the above-mentioned outside field ] is a graphite-like, and it is desirable that the diameter of the above-mentioned hollow field is 2-20nm. This carbon nanotube is indicated in detail by \*\*\*\*\* No. 500943 [ 62 to ], and the U.S. Pat. No. 4,663,230 specification. About the process, a transition-metals content particle (for example, the iron which uses an alumina as a base material, cobalt, a nickel content particle) is contacted at carbon content gas, such as CO and a hydrocarbon, and a 850-1200-degree C elevated temperature, and the method of making it grow up fibrous as an origin is mentioned [ transition metals ] in the carbon produced by the pyrolysis as indicated by the above-mentioned patent official report and the United States Patent specification. this carbon nanotube -- yes, it is marketed by the trade name of "graphite fibril", and is easily more nearly available than per- on KATARISHISU.

[0054] Although the loadings of the inorganic conductivity material in this invention constituent change with classes of conductive material, they are usually chosen from the range of the 0.1 - 100 weight section to the polycarbonate resin 100 weight section. In the case of carbon fiber metallurgy group fiber, concrete loadings have desirable 5 - 50 weight section, and, in the case of conductive carbon black or a carbon nanotube, its 0.5 - 20 weight section is desirable. If the loadings of inorganic conductivity material are under the 0.1 weight section, conductivity is not enough, and if the 100 weight sections are exceeded, difficulty generates and is not desirable to a moldability.

[0055] this invention constituent can also blend additives, such as other thermoplastics, a flame retarder, a shock-proof amelioration agent, an antistatic agent, a slipping agent, an anti blocking agent, lubricant, an antifogger, natural oil, synthetic oil, a wax, an organic system bulking agent, and other inorganic system bulking agents, with the above-mentioned polycarbonate resin further in the range which does not spoil the purpose of this invention.

[0056] Especially the combination method of polycarbonate resin and inorganic conductivity material of having said specific physical-properties value is not specified, and can adopt the method usually used with this seed technology. The resin constituent of this invention obtained in this way has the outstanding mechanical property, thermal resistance, and conductivity, and is suitable as objects for manufacture, such as components, such as various kinds of electrical and electric equipment, electronic equipment, an optical instrument, and an automobile, and housing.

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## EXAMPLE

[Example] Hereafter, although an example explains this invention, this invention is not limited to the following examples, unless the summary is exceeded.

The manufacturing method of polycarbonate resin is shown as an example of manufacture below manufacture of polycarbonate resin. In addition, analysis of the obtained polycarbonate resin was performed with the following measuring method.

[0058] (1) Viscosity average molecular weight (Mv)

Using the ubellohde's viscosimeter, 20-degree C limiting viscosity [ $\eta$ ] was measured among the methylene chloride, and viscosity average molecular weight (Mv) was calculated from the following formulas.

[0059]

[Equation 4]

[ $\eta$ ] =  $1.23 \times 10^{-4} \times (\text{Mv})^{0.83}$  ... (5)

[0060] (2) Colorimetry was performed by the end OH radical content titanium tetrachloride / acetic-acid method (method given in Makromol.Chem.88 215 (1965)). Measured value displayed the weight of the end OH radical to polycarbonate resin weight per ppm.

(3) Molecular weight distribution (Mw/Mn)

It measured with gel permeation chromatography (GPC). HLC-8020 (TOSOH CORP. make) was used for the measuring device, the tetrahydrofuran was used for the eluate, it asked by polystyrene conversion, and Mw/Mn was computed.

[0061] (4) Dynamic viscoelasticity dynamic viscoelasticity was measured as follows. 120 degrees C dried for 5 hours, press forming of the polycarbonate resin of a sample was carried out to disc-like [ with a diameter / of 25mm /, and a thickness of 1.5mm ] at 250 degrees C, and the sample for measurement was obtained. Before measurement, 120 degrees C, reduced pressure drying of the sample was carried out, and measurement was presented with it for 4 hours. Viscoelasticity measuring instrument RDA-700 (REOMETO Rix Corp. make) was used, and it equipped with the fixture of a parallel plate mold with a diameter of 25mm, and was set as 250 degrees C which is measurement temperature among the nitrogen air current with which are satisfied of the proper conditions of this device. Measurement temperature was set up by measuring the temperature in oven. The sample for measurement dried after that was set to the device, and it measured after standing by carrying out angular velocity of ten rads/s, and rotation of 10% of distortion so that the whole sample might fully serve as laying temperature. It asked for loss tangent Tandelta and complex coefficient-of-viscosity  $\eta^*$  (Pa-s) by this measurement.

[0062] According to example of manufacture 1 drawing 1, an example of the embodiment of a method which manufactures the polycarbonate resin of this invention is explained. Drawing 1 is flow sheet drawing having shown one example of the manufacture method of this invention. the inside of drawing, and 1 -- a DPC (diphenyl carbonate) tank and 2 -- an impeller and 3 -- a BPA (bisphenol A) hopper and 4 -- a and b -- a raw material mixing chamber and 5 -- for a pump and 8, as for program control equipment and 10, a catalyst flow control valve and 9 are [ a DPC flow control valve and 6 / a BPA flow control valve and 7 / a pump and 11 ] catalyst tanks. For a by-product exhaust pipe, 13a, and b and c, as for the Max blend aerofoil and 15, a vertical-type polymerization tank and 14 are [ 12 / a horizontal-type polymerization tank and 16 ] grid aerofoils among drawing. The diphenyl carbonate melt prepared at 120 degrees C under nitrogen-gas-atmosphere mind, The bisphenol A powder measured under nitrogen-gas-atmosphere mind and, respectively From a DPC tank (1), so that it may become a 197.1 mols [ /h ] (DPC/BPA mole ratio; 1.040) feed ratio from 205.0 mols [ h ] /and a BPA hopper (3) It measured with the weight feeder of a



micro motion type flowmeter and a loss in wait method, and the raw material mixing chamber (4a) adjusted to 140 degrees C under nitrogen-gas-atmosphere and was supplied continuously. Then, raw material mixed liquor was further supplied to the 1st vertical-type churning polymerization tank (13a) of capacity 100L continuously through the pump (7) at the raw material mixing chamber (4b). on the other hand, continuation supply was started for 2% of the weight of the cesium carbonate aqueous solution through the catalyst installation pipe by the flow rate of 1.6 mL/h (0.5micro mol the amount of setting catalysts : to one mol of BPA(s)) as supply initiation, simultaneously the catalyst of the above-mentioned mixture. [0063] At this time, actual catalyst control of flow was program control equipment (9), from the BPA flow rate and the amount of setting catalysts which were detected by the BPA flow control valve (6), calculated the setting catalyst flow rate and was carried out by controlling the opening of a catalyst flow control valve (8) so that this value and the catalyst flow rate surveyed with the measuring device formed in the catalyst flow control valve (8) are in agreement. It kept oil-level level constant, controlling [ controlled the 1st vertical-type churning polymerization tank (13a) possessing the Max blend aerofoil (14) at 220 degrees C under ordinary pressure and nitrogen-gas-atmosphere and, ] the bulb opening prepared in polymer discharge Rhine of the bottom of the tank section so that mean flow time becomes in 60 minutes further. Continuation supply of the polymerization liquid discharged from the bottom of the tank was carried out serially succeeding at the 2nd, the vertical-type churning polymerization tank (13b, 13c) of capacity 100L possessing the 3rd Max blend aerofoil, and the horizontal-type polymerization tank (15) of capacity 150L possessing the 4th grid aerofoil (16). As shown in the following table, conditioning of the reaction condition in the 2nd - the 4th polymerization tank was carried out, respectively so that it might become an elevated temperature, a high vacuum, and a low agitating speed with advance of a reaction.

[0064]

[A table 1]

	温度 (°C)	圧 力 (Pa)	撹拌速度 (rpm)
第2重合槽(13b)	220	$1.33 \times 10^4$	110
第3重合槽(13c)	240	$2.0 \times 10^5$	75
第4重合槽(15)	280	$6.67 \times 10$	10

[0065] Between reactions, the phenol which controlled oil-level level and carried out the byproduction in each polymerization tank was removed from the by-product exhaust pipe (12) so that the mean flow time of the 2nd - the 4th polymerization tank might become 60 minutes. Under the above conditions, it operated continuously for 1500 hours. In addition, with the melting condition, to polycarbonate resin weight, it was introduced into the biaxial extruder possessing a three-step vent-port, and the polycarbonate resin extracted from the polymer exhaust port of the 4th polymerization tank pars basilaris ossis occipitalis carried out 4.0 ppm (it is 4.4 time mol to amount of neutralization of catalyst) addition, and hydrogenation and after devolatilizing, it pelletized p-toluenesulfonic-acid butyl.

[0066] The viscosity average molecular weight (Mv) and the end OH radical contents of polycarbonate resin which were obtained were 21,500 and 500 ppm, respectively. Moreover, when the time amount the amount less than mol of  $0.06 \times 10^{-6}$  and of setting catalysts, and within  $0.1 \times 10^{-6}$  mol was computed to one mol of aromatic series dihydroxy compounds from the continuous measurement data (it is hereafter called for short "the continuous measurement data of a catalyst flow control valve") of the catalyst flow rate surveyed with the measuring device formed in the catalyst flow control valve (8), they were 96.7% of all production time, and 99.1%, respectively. Molecular weight distribution (Mw/Mn) and the value of Tan delta/eta  $\times -0.87$  were 2.3 and 4,850, respectively. This is expressed as PC-1.

[0067] In the example 1 of example of comparison manufacture 1 manufacture, program control equipment was not installed but the catalyst flow rate was carried out like the example 1 of manufacture except having fixed to 1.6 mL/h (0.5micro mol the amount of setting catalysts : to one mol of BPA(s)). The viscosity average molecular weight (Mv) and the end OH radical contents of polycarbonate resin which were obtained were 22,400 and 500 ppm, respectively. Moreover, when the time amount the amount less than mol of  $0.06 \times 10^{-6}$  and of setting catalysts, and within  $0.1 \times 10^{-6}$  mol was computed from the continuous measurement data of a catalyst flow control valve to one mol of aromatic series dihydroxy compounds, they were 89.9% of all production time, and 91.7%. Molecular weight distribution (Mw/Mn) and the value of Tan delta/eta  $\times -0.87$  were 2.7 and 2,240, respectively. This is expressed as PC-2.



[0068] The polycondensation of the phosgene was carried out to examine of comparison manufacture 2 bisphenol A by the interface method, and end closure was carried out with the phenol. The viscosity average molecular weight (Mv) and the end OH radical contents of polycarbonate resin which were obtained were 22,100 and 30 ppm, respectively. Molecular weight distribution (Mw/Mn) and the value of  $Tan \delta / \eta \times 10^{-8}$  were 2.3 and 7,550, respectively. This is expressed as PC-3.

[0069] By the combination formula shown in one to examples 1-3 and example of comparison 6 table -1, and table-2, polycarbonate resin and inorganic conductivity material were blended, and it kneaded and pelletized at the barrel temperature of 280 degrees C by single screw extruder VS-40 (product made from Tanabe Plastics). After drying 120 degrees C of obtained pellets for 5 hours, the Sumitomo Heavy Industries make, SAIKYAPPU M-2, and mold bundle force 75T are used Cylinder temperature: On conditions (300 degrees C and die-temperature:100 degree C), injection molding of various test pieces was performed and the result which does not have a line was shown for the following evaluation in table-1 and table-2 using the obtained shaping sample.

[0070] (5) Bending elastic modulus ISO The three-point bending test was performed according to the bending test method by 178.

(6) Heat deflection temperature ISO According to 75, the heat deflection temperature in 1.80MPa was measured.

(7) Conductivity (surface-electrical-resistance value)

The Sumitomo Heavy Industries make, SAIKYAPPU M-2, and mold bundle force 75T are used Cylinder temperature: The plate of 80mmx40mmx3.2mm was fabricated on conditions (300 degrees C and die-temperature:100 degree C), and the surface-electrical-resistance value was measured by Mitsubishi Chemical RORESUTA or Huy Lester (RORESUTA was used about what becomes less than [ it ] using Huy Lester about a thing with a value of 104ohms or more).

[0071] (8) Antistatic engine performance (an electrification relative value and electrification half-life) It measured about the electrification relative value and the electrification half-life using the plate of 40mmx80mmx3.2mm. Static ONESUTO meter was used for the electrification relative value and the electrification half-life, and they performed it the condition for [ \*\*\*\* voltage / of 10kV /, and \*\*\*\* time amount ] 1 minute.

(9) The 40mm x80mmx3.2mm plate of appearance of mold goods was observed visually, and it judged based on the following criteria.

O; fitness \*\*: [0072] with intense float of the x; inorganic conductivity material with which the float of inorganic conductivity material and the aggregate of inorganic conductivity material are seen a little and aggregate of inorganic conductivity material In addition, raw materials other than the polycarbonate resin used in an above-mentioned example and the above-mentioned example of a comparison are shown below. Carbon fiber: The Toho Rayon Co., Ltd. make, BESUFAITO HTA-C6-SR, the diameter of fiber of 7 micrometers, fiber length of 6mm.

Graphite: The Nippon Sheet Glass Co., Ltd. make, carbon flake #585, 340 meshes of average grain size.

Conductive carbon black: The LION make, KETCHIEN EC (oil absorption of 360ml / 100g).

Carbon nanotube: High peri-on international company make, PC/15BN (master pellet which consists of 15 % of the weight of carbon nanotubes, and 85 % of the weight of polycarbonate resin).

[0073]

[A table 2]

表-1			実施例			
			1	2	3	4
配	PC-1	重量部	100	100	100	100
	PC-2	重量部				
	PC-3	重量部				
合	炭素繊維	重量部	30	10		
	グラファイト	重量部		10		
	カーボンブラック	重量部			10	
	カーボンナノチューブ	重量部				3
	粘度平均分子量		21,500	21,500	21,500	21,500
	分子量分布 (Mw/Mn)		2.3	2.3	2.3	2.3
	$\tan \delta / \eta^{*-0.87}$		4850	4850	4850	4850
	末端水酸基濃度	ppm	500	500	500	500
特	曲げ弾性率	MPa	13,800	7,850	2,350	2,380
	熱変形温度	°C	144	143	134	133
性	表面抵抗値	$\Omega$	$3 \times 10^4$	$7 \times 10^4$	$5 \times 10^5$	$4 \times 10^5$
	帯電相対値	mV	0.5	0.3	0.6	0.1
	帯電半減期	sec	130	20	5	2
	成形品の外観		○	○	○	○

[0074]

[A table 3]

表-2			比較例			
			1	2	3	4
配	PC-1	重量部				
	PC-2	重量部	100	100		
	PC-3	重量部			100	100
合	炭素繊維	重量部	30	10		
	グラファイト	重量部		10		
	カーボンブラック	重量部			10	
	カーボンナノチューブ	重量部				3
	粘度平均分子量		22,400	22,400	22,100	22,100
	分子量分布 (Mw/Mn)		2.7	2.7	2.3	2.3
	$\tan \delta / \eta^{*-0.87}$		2240	2240	7550	7550
	末端水酸基濃度	ppm	500	500	30	30
特	曲げ弾性率	MPa	12,800	7,500	2,330	2,340
	熱変形温度	°C	143	142	132	132
性	表面抵抗値	$\Omega$	$1 \times 10^2$	$4 \times 10^2$	$6 \times 10^4$	$5 \times 10^4$
	帯電相対値	mV	0.7	0.5	0.8	0.2
	帯電半減期	sec	190	35	9	4
	成形品の外観		×	×	×	×

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is flow sheet drawing having shown one example of the manufacture method of this invention.

[Description of Notations]

1. DPC Tank 2. Impeller 3. BPA Hopper 4a, B. Raw Material Mixing Chamber 5. DPC Flow Control Valve
6. BPA Flow Control Valve 7. Pump 8. Catalyst Flow Control Valve
9. Program Control Equipment 10. Pump 11. Catalyst Tank 12. By-product Exhaust Pipe
- 13a, b, c. vertical-type polymerization tank 14. Max blend aerofoil 15. horizontal-type polymerization tank
16. Grid Aerofoil

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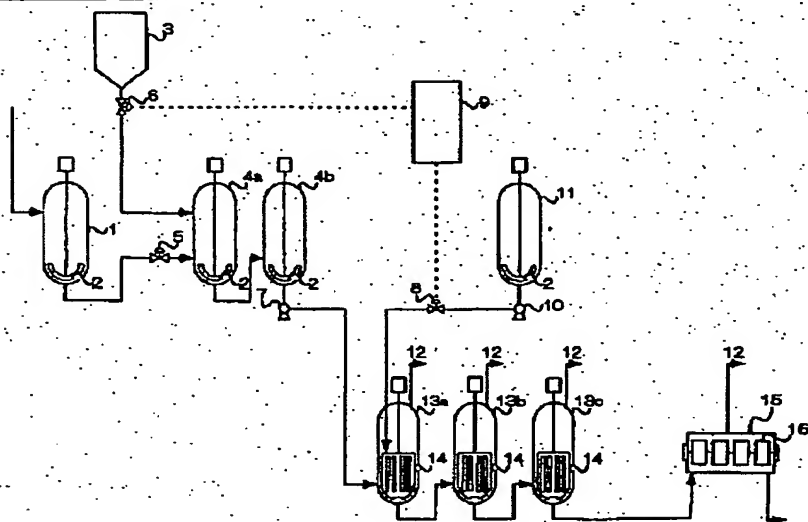
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## DRAWINGS

[Drawing 1]



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